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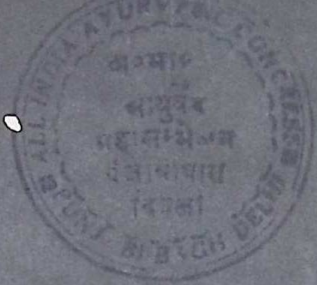

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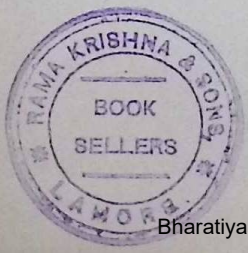

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CONVERSATIONS ON CHEMISTRY.

FIRST STEPS IN CHEMISTRY.

PART I.

GENERAL CHEMISTRY.

BY

PROF. W. OSTWALD.

AUTHORIZED TRANSLATION

BY

ELIZABETH CATHERINE RAMSAY.

12mo, viii + 250 pages, 46 figures. Cloth, $1.50.

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CONVERSATIONS ON CHEMISTRY

FIRST STEPS IN CHEMISTRY

BY

W. OSTWALD

Professor of Chemistry in the University of Leipzig

AUTHORIZED TRANSLATION

BY

STUART K. TURNBULL

PART II

THE CHEMISTRY OF THE MOST IMPORTANT ELEMENTS AND COMPOUNDS

SECOND EDITION CORRECTED

SECOND THOUSAND

NEW YORK

JOHN WILEY & SONS

LONDON: CHAPMAN & HALL, LIMITED

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AUTHOR'S PREFACE.

THE first part of this little book, which came out a year ago, had such a friendly reception on all sides that I found it a serious matter to preserve in the second volume the goodwill already rendered to me. Now my own early recollections (which have done more to supply me with a knowledge of the basis of ideas regarding the nature of substance than my later experience as a teacher did) made me feel that the question of how to introduce the quantitative stoichiometrical laws was a problem of no little difficulty. I relied on historical considerations for its solution, for as the discovery by J. B. Richter of the *law of neutrality* had, in due time, formed the first decisive step in the progressive advance of chemistry, by showing the relations of mass and number, so also the comparatively speaking simple experiments for bringing about and making intelligible the phenomena attending the neutralization of acids and bases form the foundations of a corresponding development of thought. I therefore recognized that this was the preferable course to adopt, and I hope that the means which I have chosen to represent it will not only make the access and comprehension of this phase easy to the beginner, but will also be of service in providing an available stimulus to the teacher. Personally I am absolutely convinced of the advantages of this mode of procedure over the usual one (which has to do with the law of gaseous

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volumes); and it was most instructive to me to find in this a fresh confirmation of my conviction, expressed nearly twenty years ago, that the logical development of a science follows closely along historical lines.

In other respects, this volume, being more descriptive than the former, is intended to indicate to teachers those rules of procedure which I have already expressed in other books and continue to carry out in practice. I have done my best to transgress as little as possible beyond the sphere for which the book is intended. I have, therefore, often cut short a discussion in order to resume it again later on; and I have spared no pains to explain to the pupil that, beyond the narrow limits shewn to him, science lies spread out in a vast expanse which he can only hope to tread in process of time. In this manner not only do we avoid the danger occasionally urged against elementary instruction in chemistry,—namely, that a youthful scholar, at the close of the course, imagines that he has nothing more to learn,—but, also, the student (should he be at all sensible to the influences exerted) will be early filled with that longing to pry into the mysteries of science which constitutes one of the most essential mental qualifications of a future follower of research. Indeed, to stimulate and develop this faculty of independent thought and initiative as widely as possible throughout all classes of our people is the most important task which a teacher of to-day can set himself.

Let me say that there is already a Swedish translation of the first part of this work, and an English edition will be completed immediately. My hearty thanks are due to my good friends S. Arrhenius and W. Ramsay for the trouble they have taken in preparing the above editions for the press. The first number of a Russian translation has just come out, and arrangements have been concluded for one in Dutch. Moreover, I have also to thank my numerous professional colleagues, whose criticisms on certain points in the first

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volume have been of great value. These will be carefully considered in a possible second edition. I ask their good services again for the present volume; for, as I frankly say, it is not for beginners only that I have written this book.

W. OSTWALD.

LEIPZIG, August, 1904.

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CONVERSATIONS ON CHEMISTRY.

1. CHLORINE. PREPARATION AND PROPERTIES.

M. How about what you learned of chemistry before the holidays? Have you forgotten most of it?

P. Well, it was rather curious. When we stopped I felt pretty confused and would have done badly upon an examination had you put me to that test; but when I recently looked over my note-book in which, immediately after each lesson, I had written down whatever I remembered, everything at once appeared quite clear and easy to follow. I think I could now repeat most of it correctly to you.

M. That's right; this proves that you have attended well. When we have learned much about a new subject we always require some time to digest it. Therefore it is a good thing to occupy ourselves with various matters which are related to one another; for while we are engaged with one, another is being simultaneously fixed in our mind.

P. What new things have I now to learn about chemistry?

M. We have a great choice! When we discussed the elements you always wished to hear something more about the individual substances superficially familiar to you in every-day life. That's what we shall do now.

P. I see; I have to learn about the various substances after hearing from you last term about the general laws.

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M. No; that is not the case. There is still a whole multitude of general laws with which you have not yet become acquainted, and these you must know at all events. We will now discuss, as before, the substances and their reactions; and, at the same time, the general laws which are necessary to enable us to understand the reactions.

P. I am a little afraid of those numerous general laws; we must in the long run carry so much in our heads that we shall be quite bewildered.

M. Then have you been bewildered by the general laws with which you have hitherto become acquainted?

P. No, to tell you the truth. They were for the most part so much a matter of course . . . Pardon me, I wished to say, so simple—that I could hardly even imagine that anything else was possible.

M. Quite right; if you have this impression, you have probably understood the law correctly. It will be the same with the others also, and you will learn to use them without at first being obliged to call them definitely to mind, in other words, you will be able to use them to some extent instinctively.

P. Why do you not simply say instinctively?

M. Because you must first acquire this faculty for yourself. We call instinct the inherited faculties. Let us commence with chlorine. What do you know of it already?

P. Chlorine is an element, and kitchen-salt and hydrochloric acid are compounds of it.

M. Right. What does chlorine look like?

P. I think it is a gas.

M. That is also right; but it is very different from all the gases about which you have learned so far. In the first place it is coloured, namely greenish-yellow. Then it has a very strong, unpleasant smell. It combines very easily, even at the ordinary temperature, with most of the elements, especially with all the metals. It acts on very many compounds by entering into combination with them or with

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one of their elements. Conversely, therefore, much work is required to produce it from its compounds.

P. Is it not found in nature?

M. No; a substance which enters so easily into combination, even at the ordinary temperature, could not remain in a free state, supposing it were produced anywhere.

P. Yes, that is true. Then from what can we make it?

M. From hydrochloric acid. Do you remember of what hydrochloric acid consists?

P. Let me think. I have it: of hydrogen and chlorine; indeed, it is also called hydrogen chloride. We prepared hydrogen from hydrochloric acid by removing the chlorine by means of zinc.

M. What must we do, then, to obtain the chlorine?

P. Take away the hydrogen. But with what?

M. Just think; with what can hydrogen combine?

P. I know only oxygen. But is it strong enough for that?

M. Certainly.

P. So if we lead oxygen into hydrochloric acid, is chlorine formed?

M. The process is not so simple. You know that oxygen can do nothing at the ordinary temperature. If we lead a mixture of hydrogen chloride and oxygen (we can also take air) over red-hot clay fragments which have been impregnated with copper sulphate, water and chlorine are formed according to the equation: hydrogen chloride and oxygen yield hydrogen oxid (or water) and chlorine.

P. Then what has the copper sulphate to do with it?

M. It only hastens the action: it is a catalytic agent. (I. p. 119.)

P. Can I see this?

M. I would rather not make the experiment, for by this means we do not obtain the chlorine pure, but mixed with other substances which are associated with it. In order to obtain it pure, we would better take the oxygen in the form of

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such solid compounds as give up their oxygen easily. Can you name such substances?

P. Mercuric oxide and potassium chlorate.

M. Good. Let us take potassium chlorate.

P. Why not mercuric oxide?

M. When that gives off oxygen what remains?

P. Mercury.

M. Right. Now I have told you that chlorine combines with all metals. It does so with mercury, and thus we do not obtain mercury and chlorine by themselves, but as a compound of both.

P. Then does the experiment go better with potassium chlorate?

M. Certainly; in that case whatever remains behind after the oxygen has gone away has no action on the chlorine. I take just a little potassium chlorate (as much as two pins' heads), and pour over it, in a test-tube, a little hydrochloric acid.

P. It looks like water.

M. There is water with it. Hydrogen chloride itself is a gas, but it is very soluble in water, and this solution, containing from $^1/_5$ to $^1/_3$ of its weight of hydrogen chloride, we call hydrochloric acid, and buy it under this name in the druggist's shop. Now I warm the test-tube.

P. The contents are becoming yellowish green.

M. That is the chlorine; it first of all dissolves in the liquid, but soon escapes in the form of gas. Smell it just for once, but cautiously!

P. I smell nothing.—Ah, now it comes. Phew, how abominable!

M. You now observe the reason why I have taken so little potassium chlorate: for it not only smells very bad, but it is also poisonous because it severely attacks the membranes of the nose and the lungs.—I place a polished silver coin on the mouth of the test-tube, and after some time take it away.

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P. It has become quite grey and dull, like paste.

M. The chlorine combines with the silver, which is called a noble metal because it is not attacked by the oxygen of the air, either in the cold or on heating.

P. Am I to see only this small quantity of chlorine?

M. No, we will make some more. But to do so, let us go out into the open summer-house in order that the draught of air may take away any chlorine which perhaps might escape from our apparatus.

P. Do we always do this when we work with chlorine?

M. No; in chemical laboratories we have outlets, glass cupboards with sliding doors, which are connected with a chimney that draws well, so that all the gases circulating within them escape through the vent.

P. Will you now use a large quantity of potassium chlorate?

M. No, I will use none; for to make the experiment with much potassium chlorate is not without danger. In its place I take another compound of oxygen, brown manganese dioxide. That is a mineral which we find in the earth; if we warm it with hydrochloric acid, its oxygen unites with the hydrogen of the hydrochloric acid and the chlorine is given off in a pure state, because everything else present is not volatile and so remains in the apparatus.—How must I make the experiment?

P. I think in the same way as you prepared hydrogen. (I. p. 135.)

M. Pretty good. Only we must take a thin-walled flask, as we have to apply heat in order that the chlorine may be given off. Further, we ought not to place the flask directly over the flame, else the solids lying on the bottom would get overheated and make the flask jump. That would be specially undesirable in this case, considering the chlorine.

P. So then we place a wire gauze underneath.

M. In this case that would still not be sufficient for security. Let us rather use a water-bath.

P. What is that?

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M. A small boiler of enamelled iron into which the flask fits snugly. We lay a triangle of wire on the bottom so that the flask may not stand directly on the spot heated. Also, we make the tube, through which we lead the gas, of one piece, because chlorine strongly attacks rubber tubing. We fill the flask (which for choice should not be very big, about 500 ccm.) half full of manganese dioxide in lumps, then add hydrochloric acid to completely cover them. Meanwhile the water-bath is already warm; we place the flask in it, and allow the tube for delivering the gas to dip into a dry colorless glass jar. (Fig. 1.)

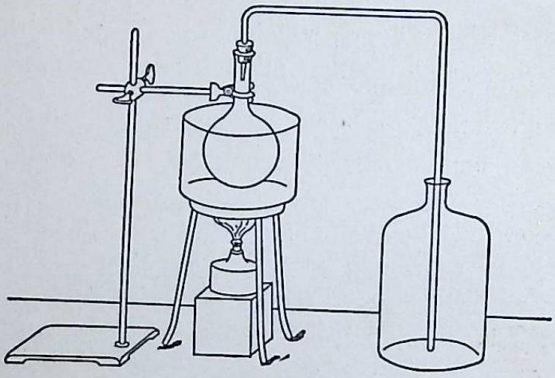

FIG. 1.

P. What is the use of this jar?

M. We will collect the chlorine in it.

P. Why do you not catch it, as usual, over water?

M. Because water easily dissolves chlorine; about 4 litres of chlorine are taken up by 1 litre of water.

P. The bottom of the jar is now becoming quite green.

M. I placed it on a piece of white paper so that you might see this more easily.

P. But it is only at the bottom.

M. Chlorine is much heavier than air, about $2^1/_2$ times. Therefore it collects at the bottom of the jar and the lighter air floats above.

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P. Yes, I see: the green colour always keeps rising.

M. When the jar is quite full we take it away and place a glass plate over the mouth. Only, place another empty vessel underneath immediately!

P. What will you do now with the chlorine? How it smells! I have already had quite enough of it.

M. I will show you that metals burn in chlorine, even at the ordinary temperature.

P. I am curious to see this. Is that gold you have there?

M. No; it is imitation gold-leaf, which consists principally of copper. I take some leaves from the small book in which it is sold, make them into a loose ball, and throw it into the chlorine.

P. It glows and smokes!

M. Meanwhile the second jar is full. I place the third underneath, and shake some powdered antimony into the chlorine.

P. What a beautiful rain of fire! What is antimony?

M. A greyish-white metal, so brittle that it can be easily powdered. We use it, mixed with lead, for printers' type.

P. Then what really becomes of the metals?

M. I have already told you: they combine with the chlorine. We call these compounds chlorides. So, what would you call the compounds formed with copper and with antimony?

P. How am I to know?

M. You only require to add chloride to the name of the metal. Thus?

P. Copper chloride and antimony chloride.

M. Quite right. Notice also that a metal can often combine with chlorine in more than one proportion. Then we add the terminations -ous or -ic to the name of the metal, according as the compound contains the less or the more chlorine.

P. So it is not the same as with oxygen, for then we should have to say monochloride and dichloride.

M. It is the same; both methods are sometimes applicable.

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How would you name both the proportions with copper and with antimony?

P. Cuprous chloride and cupric chloride; antimonious chloride and antimonic chloride.

M. Quite right. Meanwhile some more jars have been filled with chlorine. We seal them with glass plates, coated with vaseline, so that the chlorine may not escape before to-morrow. Let us stop for to-day.

2. CHLORINE AND WATER.

M. What did you learn yesterday?

P. How to make chlorine. We take away the hydrogen from hydrogen chloride with oxygen, and the chlorine remains over. Chlorine is a greenish-yellow gas, smells very bad, and combines easily with all metals without exception. Its compounds are denoted by -ous chloride and -ic chloride.—Can we also obtain chlorine in a liquid and a solid condition?

M. Certainly: we only require to compress it and cool it down. At $-33.6°$, under the ordinary atmospheric pressure, it changes into a yellowish-green liquid, which exerts a pressure at 0° of 3.7 atmospheres, and at 20° of 6.6 atmospheres. At a very low temperature it freezes to a pale-green solid. Liquid chlorine is put on the market in iron vessels capable of standing the pressure. Then we only require to unscrew the cock of such a vessel and the chlorine escapes as gas, if the cock is stood upright; as a liquid, if it is stood upside down.

P. How is that?—Ah, excuse the question, it is, of course, quite natural. But something else appears strange to me. You say that the chlorine is kept in iron vessels, and I learnt, just yesterday, that chlorine combines with all metals.

M. A good question! There is, indeed, something peculiar about this. Quite dry chlorine is by no means so eager to combine and does not affect the iron. So the chlorine contained in the "bombs", as we call the iron vessels, has only to be well dried.

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P. Then what causes this difference?

M. It is again a case of catalysis. If there happens to be no water present, the rate of combination between chlorine and iron is imperceptibly small.

P. Then has water any peculiar effect on chlorine?

M. Certainly. If chlorine and water are shaken together, the chlorine dissolves. I fill one fifth of one of the jars full of chlorine with water and shake after inserting a stopper. You see that the stopper is held fast by the pressure of the air, as the pressure inside has been removed.

P. Has all the chlorine now gone into the water?

M. By no means; only about three fourths. The pressure is lessened by the solution of the chlorine in the water, and then less chlorine is taken up. If we wished to saturate the water with chlorine, we must leave the pressure unchanged. This could be done by passing the gas through the water in bubbles. But we have dissolved sufficient chlorine for our purpose. I pour the water into a test-tube. What does it look like?

P. Like water. Perhaps a little greenish.

M. Just look into it from above, while you hold it over a piece of white paper.

P. Now it appears distinctly green. Why?

M. You must answer that yourself: we discussed quite a similar matter last term. (I. p. 9.) Think of the copper sulphate.

P. What has that got to do with it? Ah! Now I know: it is seen from above in much thicker layers.

M. Good.—If you smell the water, you will notice that it smells of chlorine. It acts on metals like chlorine-gas, and forms chlorides. We could really foretell this.

P. How?

M. The weight of chlorine which is absorbed by the water varies according to the pressure, and we can remove the chlorine again from the water by lessening the pressure.

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Thus chlorine-gas (at a definite pressure) can always exist in a state of equilibrium with chlorine-water; therefore chlorine-water can do everything that chlorine-gas does; and, of course, the product of any reaction that takes place can react again with the water already present.

P. As you express it, I can understand it quite well; but it seems to me to involve all sorts of possibilities not quite so obvious.

M. That is so; here again I have shewn you the trace of an important law of nature. But before I state it to you, I would rather wait until you have become acquainted with one or two more examples.

P. Perhaps I can find it out myself.

M. Let us consider it later on; in the mean time, we will make some more chlorine-water. To do this, we again set up our chlorine apparatus of yesterday; and in order to prepare somewhat larger quantities of chlorine-water, we lead the chlorine through a series of jars containing water, so that the gas has to bubble through one after the other. For this purpose every jar is fitted with a cork having two holes, through which there pass respectively a long and a short tube bent at right angles. (Fig. 2.)

P. But here you are taking rubber tubing to connect them.

M. That can't be helped; the chlorine soon makes it hard and liable to crack; but without rubber the apparatus would be too fragile; we can sacrifice these short, small ends.

P. Now the bubbles are already gurgling through the water.

M. Those are chiefly air. But in order not to be annoyed by the chlorine which escapes from the last jar, we lead it to the bottom of an open jar into which we shake charcoal and lime alternately. Here the chlorine is completely absorbed.

P. Then how can we see when the water is saturated?

M. We notice when the contents of the last jar become green. Then, at all events, the first jar is saturated, and we

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can move the others back and put a new jar of fresh water at the end.—We now have the first jar ready.

P. What shall we do with it?

M. Various things. Here I have a small piece of genuine gold-leaf. I pour chlorine-water over it in a small flask, and leave it to stand. After a short time it dissolves, forming gold chloride, which is soluble in water, producing a yellow solution. You see from this that even the most noble metals cannot withstand chlorine—

P. If water is present.

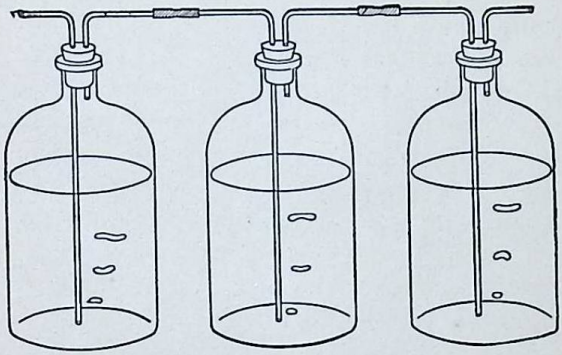

FIG. 2.

M. Very good. In another experiment I throw chlorine-water over some bright-coloured flowers. You see that they soon become white. Chlorine has a bleaching effect on many coloured substances, and it is therefore used to bleach or whiten cotton and linen fabrics.

P. Am I able to understand the reason of this?

M. Partly. These colouring matters are "organic" compounds, like wood, paper, hay. They become oxidized, i.e., burnt up, by the chlorine, and therefore the colour vanishes.

P. Burnt up? Yet chlorine is not oxygen!

M. That is explained by the water, from which the chlorine removes the hydrogen; the oxygen can then burn up the colour.

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P. Then can chlorine decompose water?

M. Yes, under certain conditions. In order to show you this I insert a cork, fitted with a short, narrow tube, into a jar quite full of chlorine-water; place it upside down in a glass, and expose the whole to sunlight. (Fig. 3.)

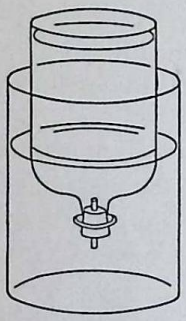

FIG. 3.

P. The water does not run out.

M. Naturally, because no air can enter through the narrow tube.

P. To be sure. But nothing is happening.

M. Wait till to-morrow; then some of the water will have run out, and oxygen will have collected in its place.

P. Then where will it have come from?

M. From the water. This is just what happens: the chlorine, under the influence of the light, combines with the hydrogen of the water and sets the oxygen free.

P. Then what has the light got to do with it?

M. It acts in the same way as a catalytic agent, by hastening the process. We call this a chemical effect of light, or a photo-chemical effect.

P. I should like to hear some further particulars about it.

M. You must wait awhile for that: in the mean time we have more important work to do. How will you recognize afterwards if the gas that is formed is oxygen?

P. With a glowing match.

M. Good. For answering that you shall see something else instructive. I have here a glass containing lime-water which has become foul by standing for some weeks. Therefore it has by no means a pleasant smell. Now add a little chlorine-water—

P. Add one bad smell to another; that will make a fine brew!

M. Just smell it!

P. I would rather not.

M. I think you wish to learn chemistry—?

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P. Let me have it.—What is this? I can smell nothing at all.

M. That is another property of chlorine: it destroys bad smells.

P. This is also caused by oxidation?

M. Quite right.

P. I would not have believed chlorine capable of this.

M. It is capable of still more. If we treat an article to which germs of disease adhere with chlorine, they are destroyed. The germs are small living organisms which make a good resistance against the usual influences of the air and so on, but not against chlorine: it kills them. So, far from proving an evil, chlorine is a real blessing: it serves as what is known as a disinfectant.

P. What does that mean?

M. To infect is to communicate, to disinfect is to free from, disease germs.—Unfortunately we cannot always use chlorine for this purpose, for it does not confine its destroying effect to the germs, but attacks everything it meets.

M. Now I understand why chlorine can be obtained for sale in iron vessels.

M. The chlorine "bomb" is seldom used for such a purpose; we generally take chloride of lime.

P. What is that?

M. It is a compound prepared by bringing chlorine into contact with lime; the chlorine is absorbed and a white powder is formed, which is usually somewhat moist, as it extracts water-vapour from the air. It can easily give off its chlorine again. Indeed, some of the chlorine keeps continually escaping into the air, as you can readily tell from the smell.

P. Why do we not use the chlorine bomb?

M. Because we only learned to make this a few years ago, and, previous to that, as we did not understand how to handle gases (such as carbon dioxide, I. p. 241) compressed into steel

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vessels, we had to prepare the chlorine for transport in another manner.

P. Why did they not simply take chlorine-gas?

M. A litre of chlorine-gas weighs roughly 3 g. We would thus have to use enormously large receptacles if we wished to despatch a few hundredweight of chlorine; but now were we to require thousands of hundredweight, it would make no difference.

P. What is chloride of lime really?

M. You are not yet able to understand the answer to that; we will return to it later on.

3. ACIDS AND BASES.

M. We have now already, several times, had to do with hydrogen chloride, and it is time you became more intimately acquainted with it. What do you know of it?

P. Its solution in water is called hydrochloric acid. It acts on zinc, setting hydrogen free. With brown manganese dioxide, chlorine is obtained.

M. What is the active agent in manganese dioxide?

P. Oxygen; for we also obtain chlorine with other compounds of oxygen. Just tell me, do all compounds of oxygen yield chlorine with hydrochloric acid?

M. By no means. I have already told you before that, for example, mercuric oxide yields none. You can bear in mind the rule that only such compounds of oxygen as part with their oxygen easily will give this reaction.—What does the word "acid" imply in the name hydrochloric acid?

P. That it has a sour taste! I have tried it myself.

M. Right. Now all sour-tasting substances have still another property by which we easily recognize them. We can buy a blue substance, called litmus. Here are some small pieces. They are angular and nearly black. I pour water over them; then, after some time, especially if kept warm, the water

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becomes a dark blue colour. Filter off this blue solution from the residue (I. p. 14); it is called litmus solution, or litmus dye, and must be kept in a flask closed with a stopper of wadding, else it will become colourless.

P. Why?

M. The reason has to do with the absence of oxygen which ensues on closing up the flask: you can not yet understand it sufficiently. I paint a piece of thin, white paper with this coloured solution.

P. I am curious to see what that is for.

M. It is for detecting acids. We can buy a piece of litmus paper like this, ready-made. Here is some cut up into small strips. If I moisten one of these strips with hydrochloric acid, what do you see?

P. It becomes red.

M. That happens with all acids; for example, with the juice of sour fruit, with lemons, apples, beer of all kinds, also with vinegar, sour milk, with everything of a sour taste.

P. Please give me some litmus paper. I would like so much to experiment with it on everything.

M. Take some.—

P. It is really the case; whatever tastes sour makes litmus red.

M. Now I will show you still a third property of acids. I have here some of the metal magnesium in the form of a powder.

P. The same as we use for the flash-light?

M. Quite right. I pour some water over it in a test-tube: nothing happens. Now I add some hydrochloric acid: a gas is given off immediately, with effervescence. What will it be? Remember that the element magnesium is a metal. How do metals act with hydrogen chloride?

P. They take away chlorine and set the hydrogen free.

M. Right! I hold my test-tube to the flame, after keeping it, for some time, lightly closed with my finger—

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P. A bang! Yes, it is hydrogen.

M. Now let us take vinegar and lime-juice, instead of the hydrochloric acid, and add magnesium powder. Gas is given off each time.

P. Yes; but much more weakly than with hydrochloric acid.

M. Therefore these other acids are called weaker acids.

P. It is curious that three such different properties as the sour taste, and the power to colour litmus paper red and always give off hydrogen with magnesium should all occur together.

M. Yes; these are characteristics of a large class of bodies which, for this very reason, are denoted by the common name of acids. It is just the same as in the case of mammals: where the properties of warm blood, an inner skeleton of bones, and a heart with four divisions, among many other diverse ones, always occur together.

P. I would really like to ask you still more about just why these properties are met with in acids all at the same time, but I can't help thinking you will put me off until later on.

M. In point of fact, you need not trouble about the matter. The last property is the most important; for it hints at the conclusion that all acids contain hydrogen, since it is given off by all.

P. Is that really the case?

M. Certainly: all acids contain hydrogen.

P. So all compounds of hydrogen are acids?

M. Oh no!

P. Indeed! Then how do you make that agree?

M. Only those compounds of hydrogen are acids which give off hydrogen with magnesium. Water, for example, which you know contains hydrogen, gives off no hydrogen with magnesium; also it neither tastes sour nor colours litmus red; therefore it is not an acid. Alcohol and petroleum behave in the same way, and both contain hydrogen.

P. Then can we detect it in some other way?

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M. Certainly; you only require to hold a cold, dry glass over the flame (I. p. 67); if it becomes dim, water is formed by the combustion; therefore hydrogen was present in the original substance.

P. How I should like to try this!

M. Quite right! Do so.—Then how would you distinguish acids?

P. Acids are compounds of hydrogen which give off hydrogen with magnesium.

M. That is quite correct.

P. Please tell me further, are all these acids different substances, or is it the same as with water,—that the differences between them come from accidental impurities?

M. You don't know what a difficult question you have put. In the mean time this answer must suffice; the acids are different substances and there are many thousands of different acids. However you require to know only about a dozen, to begin with.—But first of all I will show you still another class of bodies, the bases. The name is taken from the Latin *basis*, a foundation. They bear a definite relationship to the acids; for they can inhibit the action of the acids, and are, so to speak, their opposites.

M. I cannot understand what that means.

M. You have already seen a substance of this nature; it is caustic soda, which we used to intercept the products of the combustion of the candle. (I. p. 70.)

P. Ah, yes; I remember; the white sticks.

M. Yes. I dissolve some of it in water and put into the solution a piece of litmus paper which has been coloured red by an acid. You see, it immediately becomes blue again.

P. Can it now be turned red again by an acid?

M. Certainly; just try.

P. So we can make the paper blue and red as often as we wish?

M. Quite right. We see this still better if we use a glass

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of water which has been coloured by some litmus. I pour in a drop of hydrochloric acid; the whole liquid becomes red. Now add two drops of caustic soda solution; it becomes blue.

P. Please let me try this myself. Ah, there! I have poured in rather too much hydrochloric acid.

M. That does no harm. All you have to do is to take rather more of the caustic soda.

P. So I see. I have attended better to what I was doing; the last drop has made it quite blue.

M. Now you can make it red again with a single drop of acid.

P. A single drop? I thought I should have to take at least as much acid as I had previously taken caustic soda. Allow me to make the experiment. Yes; you are right. It is wonderful!

M. I think I know what your trouble is. Let us repeat the experiment on a somewhat larger scale. I have here about 10 g. of caustic soda; I pour some water over it, add some litmus, and then I have to pour in a pretty large quantity of hydrochloric acid before the solution will just turn red. On stirring, it becomes blue again; and, using some caution, I manage, by allowing the acid to flow in from a pipette drop by drop, to give the solution a violet colour, something between red and blue. By this treatment the liquid has become very hot. I pour it into a flat porcelain basin, heat it over the wire gauze, and keep stirring with a glass rod.

P. What is that for? It is hot already.

M. I wish to get rid of the water by converting it into vapour; we call this evaporation, and, consequently, a flat porcelain basin, such as this, an evaporating-dish. (Fig. 4.)

P. White substances are forming round the edge.

M. Yes. After some time, on continuing to stir, all the water is driven off, and a white substance remains behind; only it is somewhat coloured by the litmus.

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P. It keeps spirting up and popping.

M. Because the bottom of the dish is warmed to above 100°, and the heat is only imperfectly conducted away. If we wish to avoid this, we evaporate on a water-bath (p. 6); then the dish cannot become hotter than 100°. I have heated the basin directly over the flame in order to finish more quickly.

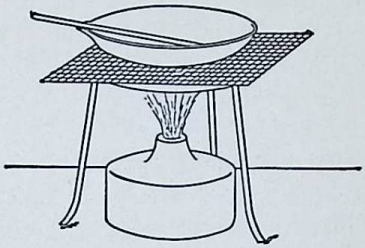

FIG. 4.

P. What have I to learn from the experiment?

M. Just taste the white substance.—You can safely attempt it.

P. It tastes salt.

M. Here is some ordinary kitchen-salt; compare them!

P. Both appear to taste quite the same.

M. Both are the same. Kitchen-salt is formed from hydrochloric acid and caustic soda.

P. That, again, is very wonderful!

M. Why?

P. Perhaps I should not really say so; but it is very odd that two such penetrating substances as hydrochloric acid and caustic soda can change into harmless kitchen-salt.

M. Yes; you see, once again, an instance how in chemical changes one set of substances disappear and others are formed. What you have seen is only one case of a great number of similar reactions. There are many more bases besides

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caustic soda, just as there are many acids. Now each base acts in a certain proportion with each acid, so that both reciprocally compensate or destroy the basic and acid properties which belonged respectively to each; and by this reaction a salt is always formed.

P. Is kitchen-salt formed each time?

M. No; kitchen-salt is only formed from caustic soda and hydrochloric acid. If you take sulphuric acid, instead of hydrochloric acid, you obtain Glauber's salt (sodium sulphate); if you take acetic acid, still another salt is formed; in short, each base forms a special salt with each acid.

P. So, then, there are many more salts than acids and bases.

M. Quite right! How many salts could you make were I to give you 10 different bases and 10 different acids?

P. Let me think. The first base gives 10 salts with the 10 acids: is that right?

M. Yes.

P. Again, the second and third bases each yield 10 salts, there are thus all together $10 \times 10 = 100$ salts. Is that really correct?

M. Yes.

P. That is quite startling: what a number of salts there must be if there are thousands of acids and bases!

M. Yes; very many are possible: but most of them are of no importance, and, therefore, they are never prepared (or, at most, only once).

P. Do they all look like kitchen-salt?

M. By no means. They are of the most different colours and forms. Also many of them are very slightly, indeed almost not at all, soluble in water. Nearly all the precipitates (I. p. 237) produced by the chemist are salts.

P. Is the white precipitate from lime-water and carbon dioxide (I. p. 237) also a salt?

M. Certainly; for lime is a base, and carbon dioxide changes into an acid on dissolving in water.

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P. Please show me this.

M. Let us take the lime first of all. I have here some ordinary mortar-lime. I mix it with as much water as will form a milky liquid: this we call *milk of lime.* A red litmus paper placed in it immediately becomes blue.

P. Yes; so it does.

M. In order to prepare the red litmus paper for this purpose we add hydrochloric acid to the litmus solution until it just becomes red, heat it to the boiling-point, when it generally becomes blue once again, then add still more hydrochloric acid until the red colour returns; and paint this on some paper.

P. Why do you not simply dip a blue piece of litmus paper into hydrochloric acid?

M. Then there would be a quantity of surplus hydrochloric acid on the paper; this would, after some time, corrode the paper; and what is still worse, a certain quantity of the base has to be used up in neutralizing all this acid before the litmus paper can be coloured blue by excess of the base.

P. I see. There is something else that I wished to ask you: has the salt no influence at all on the colour of the litmus?

M. No. I dissolve some kitchen-salt in water, colour the liquid with litmus, and divide it into two portions. I stir one with a glass rod which I have dipped in hydrochloric acid—

P. It immediately becomes red!

M. And to the other I add a little caustic soda—

P. It remains blue.

M. Now you can make an experiment yourself to prove that a very small quantity of acid makes the blue liquid red, and that some caustic soda or milk of lime changes the red to blue again.

P. Yes: it is as you say.

M. Thus we may say that a given quantity of acid yields, with a certain definite quantity of a base, a salt which does not change the colour of litmus. A solution of such a salt, which is neither acidic nor basic, we call neutral. Pure water is

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also neutral. If a trace of an acid or a base is added to a neutral liquid, such as water or a salt solution, this slight excess immediately enables litmus to assume the corresponding colour.

P. Let me now make some lime into a salt with hydrochloric acid.

M. Very well!

P. I add some litmus to the milk of lime; the liquid becomes blue. Now I pour in hydrochloric acid. But, what is this? The liquid is now just red, and it has, at the same instant, become quite clear.

M. It is a very simple matter. The basic lime is very slightly soluble in water, about 2 parts in every 1000 parts of water; on the other hand, the salt formed by the lime with the hydrochloric acid is very easily soluble in water. If all the lime has now been converted into the salt there is nothing more left over that could make the water turbid.

P. But the solution is still somewhat turbid.

M. There are impurities in ordinary lime. If we take it quite pure the liquid becomes quite clear.

P. May I taste the liquid?

M. Bravo, you have plucked up courage! Yes, you may; it is not poisonous.

P. It tastes salt, but much more bitter than kitchen-salt.

M. It is not kitchen-salt, therefore it has a different taste.

P. Can I dry this too by evaporation?

M. Yes; you may try your luck. But it is somewhat more difficult to prepare than kitchen-salt; for it is very easily soluble in water, and you will only get a sight of it after nearly all the water is driven off. Now for the carbonic acid!

P. What carbonic acid?

M. You wished to know if the precipitate from lime-water and carbon dioxide is a salt. You have seen that the lime is a base; now I shall show you that an acid is formed from carbon dioxide and water.

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P. Then is carbon dioxide itself not an acid?

M. No; for it is formed from carbon and oxygen (I. p. 228), and thus contains no hydrogen.

P. Then where does it get the hydrogen?

M. From the water. In dissolving, it unites with water; what is thus formed is called carbonic acid.

P. Now let me think:—how can I get carbon dioxide? Ah, yes, I only require to breathe out air from my lungs.

M. Bravo; you have remembered that well. But this is no good for our purpose, because exhaled air contains only a little carbon dioxide. If we take a bottle of soda-water and, after the first rush of froth is over, insert a cork fitted with a glass tube, we can lead the carbon dioxide which is given off into a glass of pure water containing a drop of litmus. Now mark what happens.

P. Yes; the water becomes red, but more violet-red and by no means so yellowish-red as with hydrochloric acid.

M. Quite correctly observed. From this we conclude that, in the case of carbonic acid, the acidic properties are very slightly developed; also the solution hardly tastes sour; and with magnesium, hydrogen is given off only extremely slowly. We therefore say that carbonic acid is a very weak acid.

P. How is that?

M. As there are clever and stupid people, so there are also strong and weak acids. You must be satisfied with this for to-day.

4. CHEMICAL EQUIVALENTS.

M. What you learned yesterday was not very easy.

P. It is as it has so often happened before. At first I thought it was very difficult and involved, but on thinking it over I found it was quite a simple matter after all.

M. Now, I am curious to know what your ideas on the subject are.

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P. I imagine the acids and bases to be boys and girls at play. If they run away in couples of always one boy with one girl, there eventually remain behind either some boys by themselves or some girls by themselves. If an acid and a base form a salt there eventually remains behind some of the acid by itself, or some of the base by itself; and that is ascertained by the litmus becoming red or blue.

M. Very good: you have effectively, and quite correctly, grasped an essential part of the question. Just let us follow this idea further. I weigh out 40 g. of caustic soda into a litre flask. Then I fill the flask at first one third full of water, shake, and wait until it is all dissolved; finally, I fill the flask nearly full of water and shake to make the contents a uniform mixture.

P. You have made a solution of caustic soda.

M. Yes, a dilute solution. Now look here at this piece of apparatus. It is a glass tube of about 1.2 cm. diameter, graduated into cubic centimeters and their tenths. The lower end of the tube is drawn out to a narrow nozzle, over which is passed a rubber tube fitted with a pinch-cock, and with a glass outlet tube drawn to a fine point. (I. p. 140.)

P. What is this used for?

M. I use this contrivance, which is called a burette (Fig. 5), to measure out exactly to one drop, desired quantities of my caustic soda solution. To do this, I fill it up to the top with the solution, which I allow to flow out through the open pinch-cock, until the surface stands at the top line, which is marked with a 0.

P. How can you do that, the surface is curved?

M. I arrange so that the lowest part of the dark arch, which you see, just rests on the stroke. (Fig. 6.) The best way to manage this is to place the burette opposite a bright window. I now measure out with a pipette, which holds 5 ccm. this quantity of hydrochloric acid, allow it to flow into a porcelain basin and add a drop of litmus.

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P. Of course, it becomes red.

M. Yes. I now allow the caustic-soda solution to flow in, and, at the same time, keep stirring. What do you see?

P. Nothing special. Yes; blue flecks now appear, but they disappear again. Aha! now you have to stir harder before the red will return.

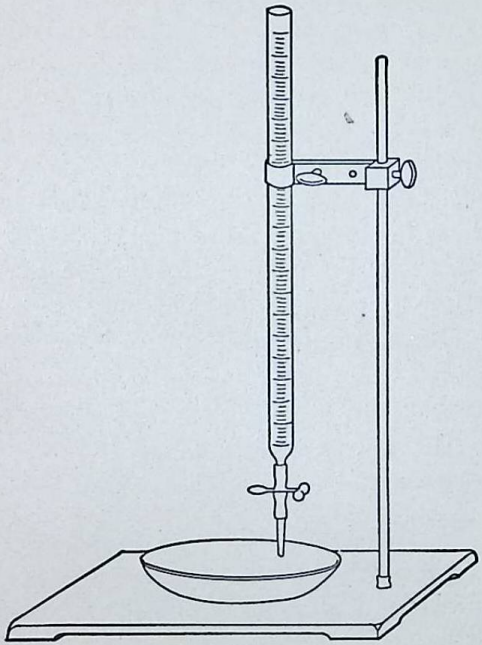

FIG. 5.

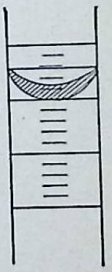

FIG. 6.

M. Very nearly all the acid is now used up, and I let the caustic soda flow in drop by drop.

P. It has become blue all at once!

M. So that was just the quantity of caustic soda necessary to form a salt with the 5 ccm. of hydrochloric acid, or, as we say, to neutralize them. I read off how much this amounts to: I have used up 23.27 ccm.

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P. Let me see. Yes, the black moon stands between the second and third stroke after the number 23, and nearer to the third. But I could not be sure that this was just 7/10 of a division.

M. You will learn with practice. But now let us reduce the hydrochloric acid so that each cubic centimeter requires exactly 1 ccm. of our caustic soda solution.

P. How will you do that?

M. It is very easy. I have what I require if I dilute 5 ccm. of the hydrochloric acid to the volume occupied by 23.27 ccm.

P. Is that so? Yes; to be sure, it is quite simple. But this yields only quite a little acid.

M. It is not difficult to remedy that; I only need to take more acid and water in the same proportions.

P. I beg your pardon; I was very stupid.

M. Because you were, calculate for me how much acid you must take in order to prepare 1 litre of correctly diluted acid.

P. 5 ccm. give 23.27 ccm., how many give 1000 ccm.?—That would be how to express it. No, better thus: for 23.27 I require 5, for 1 I require $\frac{5}{23.27}$, for 1000 I require $\frac{5 \times 1000}{23.27}$, that is 214·9. Thus I require 214·9 ccm. of hydrochloric acid. How am I to measure it out?

M. I have here a graduated cylinder which holds 1 litre up to the top stroke. You pour into it the necessary quantity. But first examine how the space between two of the strokes is divided.

P. I don't quite understand.

M. Here is the stroke denoting 700, and here is the one for 800 ccm. How many strokes are between them?

P. Nine; and the fifth is longer.

M. Yes; so, in this case, the space is divided into ten parts, and since the whole space between 700 and 800 ccm. amounts to 100 ccm., it follows—

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P. It follows that the space between each stroke represents 10 ccm.

M. Right! So you must let the hydrochloric acid flow in until it stands at the first stroke above the 200; you then have 210 ccm., and you must then add just a little more acid until it stands half way between the two strokes.

P. I would rather you added the last portion, I could not do it with sufficient accuracy.

M. Just you try; we can correct it afterwards.

P. I am afraid I have poured in too much.

M. Now just fill up with water to the top stroke. There, we now have 1000 ccm., and we pour our acid into a flask, after shaking it well. Now let us determine whether we have worked correctly.

P. I am afraid it is too late.

M. Not at all. I take 20 ccm. of my acid with another pipette, measuring them exactly in the same way as before. If we have worked correctly we must use up exactly 20 ccm. of caustic soda to neutralize them.

P. But there is no longer as much as that in the burette.

M. I again fill it up above the zero mark, and let it flow out into another dish until it stands at the mark. Now I start from 0 again; and, since I know how much I shall probably require, I allow 19.5 ccm. to flow in straight away.

P. That was too much, it is already quite blue.

M. I only require to stir to make it red again. Now some more, drop by drop: there, I have finished: I have used 20.10 ccm., so you really have taken too much acid. We must, therefore, add water.

P. That is again a matter of calculation.

M. This time it is very simple. The acid is too strong by 0.10 in every 20 ccm., so it is 1 ccm. out in 200, or 5 in 1000. Thus I just have to add 5 ccm. of water.

P. I can do that accurately with the pipette.

M. Good; but first rinse it out with pure water, else you will wash in the acid which still adheres from the previous

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use. And here notice this rule, we must always rinse out the pipettes with pure water immediately after using them.

P. Then I will also wash out the other 20 ccm. pipette which you have just used.

M. Good. Now let us shake well and again measure out the acid. But the pipette is now wet, so any acid taken up with it would be diluted, and we would make a mistake.

P. Then we must wait until the pipette is dry.

M. We do not need to; all we have to do is to rinse it out with some of the acid itself.

P. I might have thought of that myself!

M. We find it requires exactly 20.00 ccm.

P. Why do you not simply say 20?

M. Because I have also measured to tenths and hundredths. Although I have found naught there, still I must say so.—Now I will set you a task for to-morrow. Here are two more flasks, in one is sulphuric acid; in the other, nitric acid. From each make for me 1 litre of diluted acid, just in the same way as I have made the hydrochloric acid, so that equal volumes of caustic soda and acid mutually neutralize each other.

P. To do this, I first test 5 ccm. with the caustic soda, and then calculate in what proportion I must reduce it.

M. Quite right; only don't forget to keep the pipettes and the graduate clean, and to shake thoroughly each time.

M. Now, is everything correct?

P. Yes: but I hope you will not be angry with me, I made a foolish mistake at the beginning and had to pour out some of the acid because I had made it too dilute.

M. That does not matter; however, you had only to add the requisite quantity of strong acid. You can think out afterwards for yourself how you would make the calculation. In the mean time we will dissolve another base, so that it will also neutralize an equal volume of the acids.

P. It looks just like caustic soda.

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M. But it is not; it is called caustic potash. I must take much more of it for 1 litre, about 60 g.—There, the solution is ready; I take exactly 20 ccm. and test with the acid.

P. Which acid will you take?

M. That is immaterial; give me the hydrochloric acid. We use up 20.56 ccm.; so how much water must we add?

P. 20 ccm. require 0.56, 200 ccm. 5.6, so 1000 ccm. require 28 ccm. of water.

M. Right. I measure it out in the small graduate (Fig. 7); pour it in, and, in order to wash in the last traces of water, rinse afterwards with some of the solution.

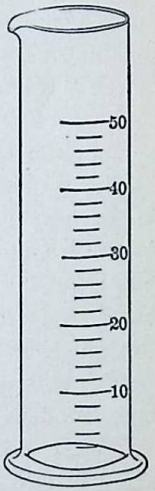

FIG. 7.

P. Another good tip which I shall note!

M. Now, what do you suppose will be the result if I test the caustic potash with the other acids?

P. I would like to believe in a certain result, but I am afraid it is foolish of me.

M. Well, what is it?

P. That the other acids also will have exactly the same effect on the caustic potash as they had on the caustic soda. But yet that cannot be, because a different salt is formed each time.

M. But yet that is the case. If there are 40.06 g. of caustic soda in 1 litre of caustic soda solution, there must be 36.46 g. of hydrogen chloride in 1 litre of hydrochloric acid solution in order that both may neutralize each other. In 1 litre of the sulphuric acid solution there are 49.04 g. of pure acid, and in the case of the nitric acid 63.05 g. On the other hand 1 litre of caustic potash solution, which contains 56.16 g. of caustic potash, neutralizes not only the 36.46 g. of hydrochloric acid, but also 49.04 g. of sulphuric acid and 63.05 g. of nitric acid. If we now draw up a table in the following manner:

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Acids.		Bases.	
Hydrochloric acid....	36.46	Caustic soda.....	40.06
Sulphuric acid.....	49.04	Caustic potash....	56.16
Nitric acid.....	63.05		

we have in each column the exact quantities of the acids or bases which are necessary, in the case of neutralization, to take the place of or to compensate each other. We call such quantities equivalents, as they are of equal value. We can thus tell from a table like this in what proportions all the given acids and bases combine to form salts.

P. Yet there is really nothing especially important about this.

M. Just reflect. Supposing I were to take some third base, say calcium hydroxide, and find that 36.46 g. of hydrogen chloride require 37.06 g. of this new base, I then know, without making a further experiment, that 37.06 g. of calcium hydroxide also form a neutral salt with 49.04 g. of sulphuric acid, or with 63.05 g. of nitric acid. In the same way, in the case of any new acid, for example acetic acid, I only require to estimate how much is required to neutralize 40.06 g. of caustic soda in order to know in what proportion it will form a salt with caustic potash and calcium hydroxide.

P. Yes; I begin to understand. We can thus enlarge the table as much as we wish, and if we have found out how much of any new acid is required for 40.06 g. of caustic soda, we know that that quantity is the same for all the bases, as they are noted on the table, and *vice versa*.

M. Certainly; only you need not take caustic soda; 37.06 g. of calcium hydroxide, or 56.16 g. of caustic potash will do just as well as 40.06 g. of caustic soda.

P. That appears to be a great, gigantic law of nature!

M. It is. We call the numbers in the table the weight equivalents of the acids and bases. So, to discover the weight equivalent of each new acid, we find how much is required to form a neutral salt with a weight equivalent of any one base;

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and the weight equivalent of a new base is found by estimating the quantity necessary to form a salt with the weight equivalent of any one acid.

P. Can you not make this clearer by some example?

M. Willingly. For 100 dollars you obtain a certain sum in British, French, German, Russian, etc., money; let us denote these equivalent quantities by B, F, G, and R. On the other hand, you can buy for 100 dollars various quantities of hay, charcoal, iron, paper, linen. Now draw up a table:

100 dollars	*h.*
B	*c.*
F	*i.*
G	*p.*
R	*l.*

in which *h*, *c*, *i*, *p*, *l* represent the corresponding quantities of hay, charcoal, iron, paper, and linen. The table shows you how much of each of the goods you obtain for the given sums of money in the various currencies. If you wish to add Italian money to the table you only require to know the price in Italian money for one of the quantities *h*, *c*, *i*, *p*, *l*. In the same way, in the case of a new piece of goods you only require to estimate the amount that can be bought for one of the sums of money in the first column; then that amount is the same for all the others. All the figures in the one column are of the same value, or are equivalent, to one another and to those in the other column.

P. Hm; it is simple enough!

5. THE WEIGHTS OF COMBINATION.

M. Repeat as concisely as possible what you learned yesterday.

P. Every acid and every base has a fixed equivalent weight; and if any acid unites with a base to form a salt, they do so in the proportion of their equivalent weights. Consequently the equivalent weights are the weights of combination.

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M. Very good; that is actually the case. But now prepare yourself for another great law of nature, one far wider still in its effect than that of which you have just spoken.

P. Can I understand it?

M. I think so, for it is very simple. *Each substance*, not only acids and bases, *has a fixed weight of combination, and if substances unite with one another and form chemical compounds, they always do so in the proportion of their weights of combination.*

P. I cannot grasp this all at once.

M. Nor do you require to; we will consume this large apple in mouthfuls. To begin with, what I have said applies to the elements.

P. To be sure, since the elements are also substances.

M. Right. For example the combining weight of oxygen is 16, that of mercury is 200. These elements unite to form mercuric oxide in the proportion of 16 parts by weight of oxygen to 200 of mercury. And if the mercuric oxide is decomposed by heat, 200+16=216 parts by weight yield 200 parts of mercury and 16 parts of oxygen. So 216 is the combining weight of mercuric oxide.

P. Actually, however, the "decomposition weight."

M. It is that also. But mercuric oxide can not only break up, but also unite with many a substance; and then the combining weight is 216. We can thus generally say that the numbers which we have previously called the combining weights could actually be named the "reaction weights", for they declare the proportionate weights in which the substances enter into any chemical reaction whatsoever.

P. Thus, properly speaking, according to this it is laid down that all substances must act on one another only in certain definite unalterable weights. But now supposing we take other weights—

M. Then that substance which is in excess of the definite proportion remains over. But you used a wrong expression;

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it is not laid down that the substances must do this, but that they behave in this way without any ceremony—of their own free will, so to speak. They understand, or can do, nothing else.

P. Please explain something more to me. You have just shewed me by your calculation that the combining or reaction weight of mercuric oxide is found by adding the combining weights of mercury and oxygen. Is that always the case? Are the reaction weights of the compounds always merely the sum of the reaction weights of the elements?

M. Certainly; that is always the case. It can never by any means be otherwise. Just suppose that mercuric oxide had quite another independent reaction weight with some other substance, say hydrochloric acid. Then we could produce the mercury again from the compound formed, and would obtain another weight to correspond with our supposition. We would thus have to take for mercury a second different combining weight. This might apply to a second, third or fourth case. Then, finally, it would be impossible to have any fixed combining weight at all, and so the law of combining weights would be suspended and worthless.

P. Yes, I see; if the law applies to the little finger, it also does to the whole hand.

M. That is not well expressed; much rather say: if a rule exists, then it must have force at all times, and on no occasion does it tolerate the slightest breach. Only think how incalculably this facilitates all chemical work: if we know the combining weights of the elements, then we know those of all their compounds; and thus we know in what proportions by weight all these substances occur in every possible chemical process which they undergo with each other. We are able to calculate what yield we can obtain from one given quantity of the substances taken, and so avoid using a needless excess of the one or the other substance: conversely we can estimate how much we must take in order to obtain a prescribed quantity of the product.

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P. Yes; here, for the first time, I correctly understand what you once said,—that a law of nature is a great help to mankind.

M. Now, we have still to learn the combining weights of all the elements which we have so far known and used. It is not necessary for you to commit the numbers to memory, but I would like you to take note of them. Besides they soon impress themselves on you by repeated use. As a preliminary, I give you this short table:

Oxygen	16.00	Chlorine	35.45
Hydrogen	1.01	Sodium	23.05
Nitrogen	14.04	Sulphur	32.06
Carbon	12.00	Mercury	200.0

P. How, actually, have these numbers been obtained?

M. We have either split up the compounds into their constituents and weighed the one or the other; or we have converted weighed quantities of the elements into compounds and, by weighing these, estimated the proportions by weight.

P. Please give me an example.

M. We can again take the case of mercuric oxide. If we spilt it up we obtain oxygen and mercury in the proportion of 1:12.50. Now we settle once for all that the combining weight of oxygen is 16, therefore that of mercury, x, is found from the equation $1:12.5=16.00:x$, $x=200.0$.

P. Yes, that is just what I wished to ask you. How did we discover the combining weight of oxygen itself?

M. That, in the same way as with the units of length and weight, has been arbitrarily fixed. Why the number 16.00 has been chosen for oxygen is a somewhat complicated story, which I will tell you another time.

P. Have all the elements been compared in this way with oxygen?

M. Not all, but most; and you have seen, in the case of the combining weights of the acids and bases that we can use

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any other substance we please, whose combining weight has been previously established, in order to estimate by its aid a new combining weight.

P. An example, please!

M. If we heat mercury with sulphur we obtain a compound of both, which is called mercuric sulphide. Here mercury and sulphur combine in the proportion 1:0.1603. Taking x for the combining weight of the sulphur we have the equation $1:0.1603 = 200.0:x$, $x = 32.06$.

P. But if we now estimate the combining weight of the sulphur directly by means of oxygen?

M. Then we obtain exactly the same number. This and many different methods of estimation have often been carried out, and always with exactly concordant results.

P. That is so simple and yet so wonderful that I can by no means properly accustom myself to it.

M. I will give you another illustration. Imagine a collection of coins, and among them German marks, British shillings, French francs, Russian roubles, etc. You can lay these coins together by twos or threes, etc., as you wish; but each of such groups has one value which amounts to the sum of the values of the single coins, and you can by no manner of means alter this value. In the same way we can prepare no other compounds than those produced by the union of the elements according to their weights of combination.

P. It is as if each element consisted of fragments purely of the same kind, just as all the marks, or all the francs, are of one kind of material.

M. That is exactly the idea that we have for long held on this subject. We suppose that each element consists of small particles which are called atoms; this name implies that these particles can not be subdivided. All the atoms of sulphur are similar to one another, as are all the atoms of mercury, oxygen, etc. Now supposing we were to place one atom of oxygen on a balance sufficiently delicate to

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weigh it, and so arranged our own units of weight that sixteen of them held one atom of oxygen in exact equilibrium, then for one atom of mercury 200.0 of such units of weight would be necessary; for one atom of hydrogen, 1.01; and so on. The combining weights of the elements can thus be regarded as the weights of their atoms, or atomic weights. In fact the former are generally called atomic weights.

P. Then is all this true?

M. No one has ever seen the atoms or weighed such a minute quantity as a single one. It is thus an hypothesis (I. p. 55) to suppose the existence of atoms. But if we do so, it affords a convenient method of observing the various applications of the law of combining weights, because the atomic theory is very simple and clear.

P. But yet we can also get on without it!

M. Certainly. But you remember that when you learned to do sums you used your fingers as a help, and that was more convenient than keeping the numbers in your head. So it is more convenient to adopt the atomic theory, so far as it applies to the abstract and universal law of combining weights.

P. Well, this law does not seem to me so fearfully difficult!

M. Nor to me either; but, to carry out his work, man rightly makes use of every facility which yields a quicker and quite as accurate a result.

P. Then are all the results arrived at by adopting the atomic theory correct?

M. Yes; so far as they concern the combining weights and matters directly associated with them. Other applications of this hypothesis are much less certain.

P. Ah, yes, I remember that we have already discussed a similar question. (I. p. 56.)

M. Since we wish, in the mean time, to apply the atomic theory in no other direction, we need not be afraid of any

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possible mistakes. I will show you another way in which we have usefully applied the atomic theory, namely, by denoting one atom of oxygen by the letter O, one atom of mercury by Hg, hydrogen by H, sodium by Na, potassium by K, nitrogen by N, chlorine by Cl, carbon by C. Then we can distinguish the compounds by simply writing the symbols of the elements side by side. Thus mercuric oxide has the symbol, or "formula," HgO; hydrogen chloride is HCl, etc.

P. Then, how were these letters chosen? Some are the initial letters of the names, but others are not.

M. They are all initial letters, only not of the English names, but of the Latin or Greek. O is the abbreviation for oxygenium, H for hydrogenium, N for nitrogenium, S for sulphur, C for carbo. Natrium is the Latin for sodium, and in this case the symbol ought also to be N; but, in order not to confuse it with the N of nitrogen, we have added the a. All the symbols are formed in a similar manner.

P. What have we gained by this?

M. A very great abbreviation. If we see that HCl is the formula for hydrogen chloride, we understand from these brief symbols not only that this substance is formed from hydrogen and chlorine and can be split up into these elements, but also that both the elements combine, or are present, in the proportion by weight of 1.01:35.45, that no other elements than these can be produced from hydrogen chloride; and finally, that the combining weight of hydrogen chloride for every reaction that we can possibly design amounts to $1.01+35.45=36.46$. That is a good deal for a symbol which only consists of three letters.

P. Yes; that is true. But we do not actually require the atoms for this purpose, since I already knew about this from the law of combining weights.

M. You are quite right. But owing to the complicated history of this subject, we approached all these conclusions with the idea of the existence of atoms and afterwards found

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TABLE OF THE COMBINING OR ATOMIC WEIGHTS OF THE ELEMENTS

Aluminium	Al	27.1	Neon	Ne	20.
Antimony	Sb	120.2	Nickel	Ni	58.7
Argon	A	39.9	Niobium (Columbium, Cb)	Nb	94.
Arsenic	As	75.0	Nitrogen	N	14.04
Barium	Ba	137.4	Osmium	Os	191.
Beryllium (Glucinum, Gl)	Be	9.1	Oxygen	O	16.00
Bismuth	Bi	208.5	Palladium	Pd	106.5
Boron	B	11.	Phosphorus	P	31.0
Bromine	Br	79.96	Platinium	Pt	194.8
Cadmium	Cd	112.4	Potassium	K	39.15
Cæsium	Cs	132.9	Praseodymium	Pr	140.5
Calcium	Ca	40.1	Radium	Ra	225.
Carbon	C	12.00	Rhodium	Rh	103.0
Cerium	Ce	140.25	Rubidium	Rb	85.4
Chlorine	Cl	35.45	Ruthenium	Ru	101.7
Chromium	Cr	52.1	Samarium	Sm	150.
Cobalt	Co	59.0	Scandium	Sc	44.1
Copper	Cu	63.6	Selenium	Se	79.2
Erbium	Er	166.	Silicon	Si	28.4
Fluorine	F	19.	Silver	Ag	107.93
Gadolinium	Gd	156.	Sodium	Na	23.05
Gallium	Ga	70.	Strontium	Sr	87.6
Germanium	Ge	72.5	Sulphur	S	32.06
Gold	Au	197.2	Tantalum	Ta	183.
Helium	He	4.	Tellurium	Te	127.6
Hydrogen	H	1.008	Terbium	Tb	160.
Indium	In	114.	Thallium	Tl	204.1
Iodine	I	126.85	Thorium	Th	232.6
Iridium	Ir	193.0	Thulium	Tu	171.
Iron	Fe	55.9	Tin	Sn	119.0
Krypton	Kr	81.8	Titanium	Ti	48.1
Lanthanium	La	138.9	Tungsten	W	184.0
Lead	Pb	206.9	Uranium	U	238.5
Lithium	Li	7.03	Vanadium	V	51.2
Magnesium	Mg	24.36	Xenon	X	128.
Manganese	Mn	55.0	Ytterbium	Yb	173.0
Mercury	Hg	200.0	Yttrium	Y	89.0
Molybdenum	Mo	96.0	Zinc	Zn	65.4
Neodymium	Nd	143.6	Zirconium	Zr	90.6

by experiment that it was justified by the actual facts. These have provided, to a certain extent, a confirmation of the atomic theory; of course, more a confirmation of its utility than of its correctness.

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P. Is not this the same?

M. No. For example, in daily life it is quite useful to assume that the sun and all the stars revolve once in the twenty-four hours round the earth, and we therefore speak of the sun rising and setting. Yet we know that astronomers hold that this assumption is not correct; but, on the contrary, that the sun and stars stand still and the earth revolves on a north and south axis.—Let us now leave this subject; and, in conclusion, I will give you another table in which all the accurately known elements are entered, with their symbols, and their combining or atomic weights (p. 38).

6. MULTIPLE PROPORTIONS.

M. Well, did you find it easy to grasp what you learned yesterday?

P. Each element has a combining weight, and the combining weight of a compound is the sum of the combining weights of its elements.

M. Right. And what do these numbers mean?

P. That all combinations between substances take place only in such proportions by weight as are denoted by the proportion of their combining weights.

M. Not only the combinations, but also the decompositions, and all chemical changes whatsoever.

P. And then I have also learned how to write the formulæ of the compounds. We simply place the symbols of their elements together.

M. And what purpose do the formulæ serve?

P. They denote the composition of the compound.

M. Quite right. I will show you still another similar use for them. We can also write chemical equations by means of these formulæ. You remember how I already once before (I. p. 89) wrote such an equation in words,

mercuric oxide = mercury + oxygen.

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Using formulæ this is expressed thus:

$$HgO = Hg + O.$$

P. That is certainly much shorter.

M. And it means much more; for if you write the combining weights against the symbols, you know the proportions by weight in which mercuric oxide is formed or decomposed.

P. Can we write such equations for all chemical processes?

M. Yes. Both sides of a chemical equation must correspond in the number and character of the symbols of the elements, else it is not correct.

P. Why?

M. As an expression of the law of the conservation of the elements. (I. p. 92.) You know that it is not possible to change one element into another, or one compound of a distinct composition into elements of a different kind. This is expressed by the law which I have just given you.

P. Then if we write a chemical equation so that we have the same elements on the right as on the left side, is it always correct?

M. That is rather a sly question, and I must give the answer, no. It is by no means feasible for every element to combine with every other; so, much fewer combinations take place than are admissible within the limits of the ascertained laws. Besides, we cannot yet effect all the chemical changes conceivable.

P. Why not?

M. Probably because our means are limited. We are still, for instance, far from obtaining the highest possible temperatures and pressures. But you will have enough to do to become acquainted only with the substances which can be easily obtained; for I must now tell you that I have stated the circumstances more simply than they actually are.

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P. Perhaps the law of combining weights is not exact?

M. No; it is the most exact of all we know. No deviations from it have ever yet been observed, in spite of the use of the most accurate methods of testing.

P. Then what else can you mean? You have told me yourself that deviations are not possible in these cases.

M. Neither they are; but there can be larger multiples. Do you remember the compounds of carbon and oxygen? What are they?

P. Carbon monoxide and carbon dioxide, the first has less, the last more oxygen.

M. Very good. Now consider this fact in relation to the law of combining weights. Does nothing strike you?

P. No.

M. Just write the formula for carbon monoxide.

P. I must, I think, write OC.

M. We usually write it CO; but either is correct. And now carbon dioxide.

P. Hm—yes—how is that possible? We must not give it another formula! How are we to manage it?

M. That, you see, is the point. You have till now taken it for granted that one combining weight of an element always unites with one combining weight of another; and I have not troubled you about this in order to enable you to understand the whole subject more easily. But now you must learn that in addition to the proportion of 1:1 there occur many others, 1:2; 1:3; 2:3; and so on. The same thing happens if three or more elements unite. Then we have, as well as the proportion of 1:1:1, others such as 1:2:1; 1:2:2; 1:2:3; 1:2:4; and so on.

P. Alas, then all the beautiful simplicity is again lost.

M. Not quite, for these new numbers, or factors, are themselves simple. If A, B, C, etc., are the symbols of certain elements, the formulæ of their compounds are represented by $mA+nB+pC$, etc., and then the letters m, n, p, etc., de-

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note quite small numbers. We shall not have under consideration any above seven.

P. How then is carbon dioxide represented?

M. I have already told you before that it contains double as much oxygen as carbon monoxide. Now this has one combining weight of oxygen, so the other has two.

P. And the formula?

M. We must write it in some such way as C, 2O. However we usually place the factor after, and above or below, the symbol of the element, so we write CO_2, or CO^2. We will use the form CO_2.—Now just calculate out for me the composition of carbon dioxide.

P. How can I?

M. Use the table on p. 34 or that on p. 38.

P. Hm? Yes, I know. C is 12.00 and O is 16.00, thus 2O is 32.00; so we have 12 parts by weight of carbon with 32 of oxygen.

M. Quite right; and thus it is with all other compounds. Here you have a table giving the formulæ of differently compounded substances with which you have become more or less acquainted. You can calculate out for yourself their composition with the aid of the table on p. 38.

Mercuric oxide, HgO	216.00
Carbon monoxide, CO	28.00
Kitchen-salt, NaCl	58.50
Hydrogen chloride, HCl	36.46
Carbon dioxide, CO_2	44.00
Water, H_2O	18.02
Manganese dioxide, MnO_2	87.00
Caustic soda, NaOH	40.06
Caustic potash, KOH	56.16
Calcium hydroxide, CaO_2H_2	74.12
Nitric acid, HNO_3	63.05
Sulphuric acid, H_2SO_4	98.08
Potassium chlorate, $KClO_3$	122.60

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P. I have calculated out the figures; and I wondered how they were able to find out the formula which enabled them to estimate the composition without further trouble.

M. I do not understand you.

P. I mean, how did they manage to make out the formula so that it could account for the correct composition?

M. I am still not quite clear as to what you are thinking of. You do not surely mean that they knew the formula before they knew the composition?

P. That is just what I mean. You have given me the formula, and from that I have calculated the composition.

M. But here you have reasoned yourself into a big mistake! In every case, the formula can only be established after we have made certain of the composition by experiment. The formula is nothing more than a shorter and more distinct expression of the empirically ascertained composition.

P. Ah, so it is the reverse of what I thought! Yes; I understand now.

M. The chemical formula is by no means a magic symbol which calls forth something that was not there before. It is only when we have made the necessary quantitative experiments that we can, if at all, think out how to draw up the formula.

P. Yes; now I see clearly. Once again the question is much simpler than I thought at the beginning.

M. It will be best for me to show you exactly how we make such researches. We have two methods, the synthetical and the analytical. In the first, we start with the elements and build up the compound from them; in the other, we start with the compound and decompose it into its elements. Building up is called synthesis; breaking down, analysis. Take mercuric oxide, as an example. If we weigh out some mercury; pour over it some nitric acid; evaporate to dryness; and cautiously heat what remains; we obtain mercuric oxide as a residue.

P. How does that happen?

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M. Look at the formula for nitric acid (p. 42); it contains much oxygen, and gives it up, by the process described, to the mercury. In doing so, all sorts of intermediary substances are formed, but they do not concern us because at the end they disappear. Now, if you have first of all weighed the mercury, and afterwards weigh the mercuric oxide, the increase in weight is that of the oxygen. Then you can draw up the recognized proportions (p. 34).

P. But you have not yet weighed the oxygen!

M. I have not weighed it directly; but since I know that mercuric oxide consists of mercury and oxygen, I can calculate the weight by considering how much the mercury has increased in weight.

P. Yes; I understand. This is the synthetical treatment.

M. Right. The analytical is carried out in this way: we weigh some mercuric oxide; heat, until it splits up into oxygen and mercury; collect the latter, when it cools; and weigh it. The decrease in weight is that of the oxygen.

P. May we then say that this weight is accurate?

M. Certainly; we rely for its accuracy on the law of the conservation of mass, which provides that the weight of the mercuric oxide must be the same as the sum of the weights of the mercury and oxygen. If we know two of these three quantities we can always calculate the third.

P. Yes, that's it. I have always felt a little uneasy, because I had not considered this law.

M. Let us take yet another important example; water and hydrogen. Here we acted as follows: hydrogen was led over weighed copper oxide which gave up its oxygen to the hydrogen, and formed water. This was collected and weighed. What was lost by the copper oxide was thus the weight of the oxygen, and the difference between this weight and that of the water is the weight of the hydrogen.

P. Please write it down for me!

M. The equation is $CuO + 2H = Cu + H_2O$. Three of these

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quantities are known, and we have to deal with the CuO so that it will yield $Cu+H_2O$, and since the right and the left of the equation must coincide, we make the calculation with 2H.

P. Another case of the law of the conservation of mass!

M. Yes, it is made use of again and again.

P. Then why do we not also weigh the hydrogen?

M. That is very difficult, because it is so light a substance. We have to use very large vessels, even for a small quantity; 1 g. of hydrogen occupies the volume of 11 litres.

P. So that is the reason!

M. Yes, the more convenient method of estimation is usually the more accurate. Now in this experiment they found the following figures:

Copper oxide	60.369
Copper	49.537

Consequently

Oxygen	10.832

Further,

Water	12.197

less

Oxygen	10.832

gives

Hydrogen	1.365

Thus 1.365 g. of hydrogen have united with 10.832 g. of oxygen. Since H_2O is the formula for water, two combining weights of hydrogen are present with one of oxygen, and we have the proportions

$$2x:16=1.365:10.832$$

where x is the combining weight of hydrogen, and therefore

$$x=1.01.$$

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P. Now, I think I understand everything.

M. I must, of course, add that the question becomes still more involved if we have to investigate more complex compounds, but the principal is the same.

P. Yes; then, perhaps, you will now be able to explain to me how the two comes into the formula of water. That of mercuric oxide has no two.

M. You mean that we could make the combining weight of hydrogen equal to the quantity which has united with 16 parts of oxygen, as we did in the case of mercury?

P. Yes, that is exactly what I mean, only I could not express it so clearly.

M. It just depends on the circumstance that several compounds can be formed from two elements. Think of carbon monoxide and carbon dioxide. If we take the former as a basis, the combining weight of carbon comes to 12; for in carbon monoxide 16 parts of oxygen are present with 12 parts of carbon. But if we take carbon dioxide, which consists of 12 parts of carbon and 32 parts of oxygen, then 6 parts represent the quantity of carbon in combination with 16 parts of oxygen, and we have to take 6 as the combining weight of carbon.

P. And then what becomes of the carbon monoxide?

M. That would obtain the formula C_2O.

P. Hm, yes. In this way we have given the preference to carbon monoxide as a basis. Then what right have we to do so?

M. To begin with, we have an equal right to choose the one or the other. Now, taking the whole field of chemistry into consideration, we find it better, that is simpler and consequently more suitable, to say that $C=12$.

P. I cannot yet quite understand.

M. Nor could you even with the best will in the world, because you would have to be already in possession of information which you will only acquire later on.

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P. And is it the same in the case of hydrogen?

M. Yes. It has been settled that, taking it all in all, it answers the purpose best to consider that H=1.01, and to write water as H_2O. Previously we did otherwise and doubled the combining weight of hydrogen, so as to be able to write water as HO; but it did not stand the test, and we determined on the present formula because we have been able to gain in exchange for this small complication an important simplification in many other instances.

P. It is a pity that I am not yet able to see a single instance of this.

M. We can discuss one case of this kind now. Just calculate the combining weights of the acids and bases whose formulæ I have already given you (p. 42), and compare them with the weights that we required for our equivalent solutions (p. 30). Write all your results in the form of a table.

P. I obtain:

	Combining Weight.	Equivalent Weight.
Hydrogen chloride	36.46	36.46
Nitric acid	63.05	63.05
Sulphuric acid	98.08	49.04
Caustic soda	40.06	40.06
Caustic potash	56.16	56.16
Calcium hydrate	74.12	37.06

These values are mostly the same.

M. I had already mentioned to you the above combining weights before you knew about them. The figures applicable in the case of the formation of salts are just a special instance of the universal law.

P. Yes; I have made that tally in almost every case. But with sulphuric acid and calcium hydrate it does not agree; the old numbers are only half the new. I cannot understand that.

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M. Do you remember our definition of acids? It referred to hydrogen.

P. Yes, acids are compounds of hydrogen which lose their hydrogen by the action of magnesium.

M. Quite right. Hydrochloric acid and nitric acid contain just one combining weight of hydrogen in their formula. Sulphuric acid—

P. Contains two. What does this mean?

M. If you wish to take a quantity of sulphuric acid that will contain as much hydrogen as there is in one combining weight of hydrochloric acid or nitric acid, you must take just one half of the combining weight of sulphuric acid.

P. I do not yet understand perfectly.

M. Acids can be taken in equivalent quantities so that each gives off equal quantities of hydrogen with magnesium. If we wished to write the formula of sulphuric acid so that it only contained one combining weight of hydrogen, we would have to write it $HS_{1/2}O_2$. Now we have laid down a rule never to write fractions of the combining weights. Thus, then, it is necessary to write the formula of sulphuric acid with 2H. Thence it follows that one combining weight of sulphuric acid contains two equivalents (p. 30); thus the equivalent weight is equal to one half the combining weight.

P. So the case is similar to that of carbon monoxide and carbon dioxide.

M. To a certain extent.—The same explanation also does for the calcium hydrate. Write the symbol for the halved formula.

P. $Ca_{1/2}OH$.

M. If you compare this with caustic soda, NaOH, and caustic potash, KOH, you see that equivalent quantities of the bases are those which contain one combining weight of hydrogen and oxygen. But if we wish to do away with the factor $^1/_2$, we must write calcium hydrate as CaO_2H_2,

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or $Ca(OH)_2$, and its combining weight becomes equal to twice the equivalent weights of caustic potash and caustic soda.

P. Then does $(OH)_2$ thus mean the same as O_2H_2?

M. Yes; whatever number is placed outside refers to every symbol in the parenthesis.

P. The OH seems to be a regular characteristic of the bases, just as the H is of the acids.

M. We call OH the hydroxyl group: the name is formed, as you see, from the Grecian designations of its constituents. Your remark is quite correct; all bases contain hydroxyl, i.e., hydrogen and oxygen, in equivalent combining weights.

P. So, are all substances bases which contain O and H?

M. Your converse deduction is not admissible; we know of many substances, for example water, which contain O and H, and yet are not bases.

P. How else, then, do we recognize bases?

M. By this; that they form salts with acids, and thereby cause the properties of acids to disappear or become neutralized. (P. 20.)

P. But they always contain hydroxyl?

M. Yes. Now just set down for me the chemical equation for the formation of sodium chloride or kitchen-salt. You have seen that it is made from hydrochloric acid and caustic soda; you will find their formulæ on p. 42.

P. $HCl+NaOH=NaCl$.

M. Wrong.

P. Yet those are the correct formulæ?

M. Yes, but the law of the conservation of the elements is broken. We must have on the right and left the same number of the same elements. What is there on the left that you have not on the right?

P. An H, an O, and another H.

M. $2H$ and an O. Now no gas was given off during the neutralization, so neither the hydrogen nor the oxygen can

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be in a separate condition. Consequently they must have formed a compound which is not gaseous.

P. That I understand.

M. Now, look at the table; what compound has the composition H_2O?

P. Water!

M. Right. Complete the equation by adding this.

P. $HCl + NaOH = NaCl + H_2O$.

M. That is right. You see from this that we can predict, by means of the laws of chemistry, what must be formed, even although we do not know the complete equation.

P. Yes; that is astonishing. Then can we rely on such a calculation?

M. We can in such simple cases as this; but in complicated instances the equations generally become capable of several interpretations. But in each case we must prove by experiment that the conclusion we have drawn from the formulæ is correct.

P. Can I see how you do that in this case?

M. Yes, if we lead hydrogen chloride gas over caustic soda, they act on each other, with the evolution of great heat, and the water formed is given off as vapour which we can condense to liquid water.

P. Please do it now before me!

M. I require for this purpose hydrogen chloride gas, and we have not yet discussed its preparation. We will make it later on and carry out this experiment with it.

7. THE ATOMIC THEORY.

M. What new thing did you learn yesterday?

P. That the elements can unite together not only in the simple proportion of their combining weights, but also in other proportions.

M. And what is the nature of these other proportions?

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P. It is as if the combining weights were 2, 3, 4, or more times greater than they really are.

M. That is not quite well expressed; for it is not well for us to call the combining weights in use the real ones, as compared with those which are present in the compounds here referred to. These numbers represent the proportions by weight in the reactions, and under these circumstances the one is as real or unreal as the other.

P. Is that so? I thought that these numbers had a deeper significance which enabled us to explain the law of combining weights.

M. What then requires explanation in this law?

P. Really nothing; but I thought there might, perhaps, be something especial in the background behind such a remarkable law.

M. Just so! Of course, this is quite a childish idea, like that of the peasant who, when they tried to explain the locomotive to him, said: I understand all that very well; but, then, where really is the horse which drags all these waggons?

P. Ha, ha, ha! He was stupid!

M. Not so very. He had no experience of the fact that we can set a waggon in motion otherwise than with a horse yoked on in front, and therefore he supposed that he would be able to understand the locomotive only after they had shown him the hidden horse. In point of fact, chemists have for the last hundred years assumed that there is such a hidden horse in the law of combining weights.

P. A horse! What does that mean?

M. I speak figuratively. I mean that formerly it was necessary, just in the same way for people to assume some such cause as regards the law of combining weights; because, without it, they could not put into expression the existence of such a law,—just as the peasant could not express to himself the idea that a train can get in motion without a horse.

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P. Then, what does the chemical horse look like?

M. You know already, it is the atom. (P. 35.)

P. I did not think of that! And yet we were able to explain only the simple compounds with it; where there was one atom of one element and one atom of another element.

M. Certainly not; what is there to prevent us from admitting several atoms of the one or the other element? In the case of carbon monoxide, CO, there is one atom of carbon and one of oxygen; in carbon dioxide, CO_2, there are two atoms of oxygen to one of carbon.

P. Yes; that works. But what has this to do with our law?

M. Two atoms of oxygen weigh just twice as much as one.

P. Ah, I understand. Once again this is so simple that I did not see it purely on account of its simplicity. But, then, all atoms of oxygen must weigh just the same. Have we the right to assert this?

M. Let us think this matter over.—Just suppose that sulphur, for example, consists of small particles all of the same substance, would the particles have to be quite similar; or could they differ, say in size?

P. I don't know why they should not. Grains of sand are of different size.

M. How do you discover that?

P. Well, I can sift the sand; then the small grains go through and the large remain behind.

M. Very good: you thus assume that there are two kinds of sand, coarse and fine. Just suppose you had a sieve fine enough to effect a similar separation in the case of the sulphur atoms.

P. Then I would assume that they were coarse and fine.

M. Are they?

P. I don't know.

M. Yet, you must know. What have I told you of the properties of a given substance?

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P. That they always are the same, no matter whence we may obtain the substance.

M. Quite right: therefore what must you conclude regarding the separation of the coarse and fine atoms?

P. That we cannot separate them.

M. That is a possible conclusion; but the other is that all the atoms of sulphur are similar to one another, so that there can be no "fine" or "coarse" sulphur at all in this sense.

P. That is clever! We can thus prove that all the atoms of sulphur are similar to one another!

M. Slowly, slowly! You drew much too hasty a conclusion! We can only prove that, if sulphur consists of atoms, these atoms must be assumed to be, at all events, similar to one another.

P. Yes—to be sure, that is different. I came across this proverb the other day: the man who invented the "if" and the "but" would have no difficulty in making gold out of chopped straw.

M. You have made an apt quotation. It means that we can draw most remarkable conclusions from arbitrary assumptions. But let us see what more we ought to say of the atoms.

P. Ought? We ought to say whatever we like of such fanciful objects.

M. Yes, if we had to deal with a mere fancy. But here we must see that our assumption does not contradict our experience of the discovered laws of nature.—Now, we found in the case of sulphur that its atoms, if they exist, must all be similar to one another; else we could be able to separate a given sample of sulphur into portions with somewhat different properties.

P. Please—not so quick! Supposing there was not a sieve sufficiently fine for the atoms, your conclusion would not necessarily be correct.

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M. Quite a proper remark. But sifting is not the only means of separating coarse and fine sand; we can do it also by washing, by winnowing, etc. On the other hand, since not one single method is known of separating from sulphur, or from any other pure substance, portions having different properties, my conclusion is not absolutely proved, but still is made very probable.

P. So it is not actually proved!

M. Consider; all the laws of nature are in a similar condition; each of them holds good only so long as no fact is observed to contradict it.

P. So, then, are we as certain of the atoms as of the laws of nature?

M. Not quite; for the laws of nature are not based on an arbitrary assumption, like the atomic theory, but express definite relations between measurable and tangible quantities. But let us return to the atoms, and further develop the conclusion which we drew in the case of sulphur.

P. I have already noticed that we must assume for all substances that each contains only exactly similar atoms.

M. Good. But if the atoms of a substance are similar, they are also equal in weight.

P. But that must be very small!

M. Small or great, it must have a definite value which is the same for all the atoms of a given substance.

P. Yes; I see.

M. Now the law of the conservation of the elements goes further. To express this, we further assume that the atoms of the elements continue to exist in those of their compounds, so that the atoms of the compounds are composed of the atoms of the elements. Then we have only one way of representing the elemental composition of a given compound, namely, by those elements whose atoms form the atom of the compound.

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P. Yes; that is true! And if two elements give several compounds?

M. Then the elementary atoms, which take part in building up the compound atoms, differ in number. If one atom of carbon monoxide is built up of one atom of carbon and one atom of oxygen—

P. Then carbon dioxide contains one atom of carbon and two of oxygen.

M. I see; you have grasped the subject.

P. Yes, I just require to consider that in chemical formulæ each symbol of an element stands for one atom.

M. Bravo, you have understood quickly. I see that the atomic theory has something very accessible about it.

P. I had already, once before, heard something of it; but I could not then understand.

M. Now you see that the weights of the atoms must stand in the same proportion to one another as the combining weights of the elements. Therefore, we also call the latter atomic weights.

P. I do not know—everything does not yet seem clear to me. Since we are never certain if there are atoms, we cannot estimate their weight.

M. Your doubt arises because we express ourselves too concisely. We must say instead of atomic weights, "proportions of the weights of the atoms," or "relative atomic weights"; and, as an example of fuller expression, let us say that the proportion of the weight of one atom of hydrogen to one atom of oxygen is as 1.01:16.00. The same proportion holds good between the weight of as many atoms of hydrogen as you please and just as many oxygen atoms. So, if there are atoms, their weights must be in the proportion of their combining weights; for, otherwise, we could not assume that the compounds can be represented by a simple placing together of the elementary atoms.

P. One other thing you must explain to me: if the com-

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pounds are composed of the atoms of the elements, their properties must be met with again in the compounds. But, yet, that does not appear to be the case; I cannot discover the properties of carbon in carbon dioxide; the latter has, perhaps, some of the properties of the oxygen, but yet not all.

M. You are quite right. Except the weight (and the dimensions), the properties of an element are not met with again, exactly as before, in its compounds.

P. That's a pity!

M. Still, I must add that sometimes even the same element which thus ought to consist of the same atoms, seems charged with different properties. Just let me remind you of charcoal, graphite, and diamond.

P. Yes; these are all carbon, only they contain different amounts of energy.

M. You have taken good note of that.

P. Well, is the same the case with the atoms?

M. We assume that their properties depend on how the different atoms are arranged in reference to one another in the compound. If you have two atoms, they can be nearer or further from each other; and if you have three or more, their relative position can differ in many ways. Now, if we assume that the properties depend on this, we can consider that all sorts of possible properties (whether met with in the elements or not) are conceivable in their compounds.

P. But carbon is nothing but one element!

M. What do you mean?

P. I mean that what you have just said does not explain why carbon has different forms.

M. So, that's what you say! We here obtain help from the theory that the atoms of carbon unite, to form groups, in various numbers which cling together similarly to the different atoms of the compounds. We call such groups molecules, and we assume that charcoal, diamond, and

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graphite consist of molecules compounded of carbon atoms different in number and arrangement.

P. Then how many atoms of carbon are there in the molecules of charcoal, diamond, and graphite?

M. We do not know that yet.

P. Then the whole subject does not appear to me to be of much importance!

M. In this case, it is of no especial importance. But you will see later on, when we come to consider the gases more minutely, that the idea of a "molecule" has quite a definite importance and use. The case is similar to that of the atomic theory.

8. THE LAW OF GASEOUS VOLUMES.

M. Now we must again return to our hydrogen chloride; we have still very much to learn about it. What are the proportions of its constituents?

P. H has the combining weight 1.01, and chlorine has 35.45; so 36.46 parts of hydrogen chloride contain 1.01 parts of hydrogen and 35.45 parts of chlorine.

M. Quite right; what sort of parts are they, by weight or by volume?

P. Parts by weight, to be sure.

M. Right. But in what proportions by volume will both gases combine?

P. We cannot know that from these figures!

M. No; but we can calculate it from them. To do this we only require to know what space 1.01 g. of hydrogen and 35.45 g. of chlorine occupy.

P. Yes; but how are we to find that out?

M. If we measure the volume as well as the weight of a certain sample of hydrogen and another of chlorine, then we can easily calculate what space those weights occupy.

P. Please reckon it out for me!

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M. You discovered (I. p. 139) that one litre of hydrogen weighs roughly $\frac{1}{11}$ g.; accurately 0.0901 g. So if 0.0901 g. occupy the space of 1 litre, what space will 1.01 g. of hydrogen occupy?

P. 1.01/0.0901 = 11.210 litres.

M. Right; but let us confine ourselves to the first decimal, thus 11.2 litres. Now, in the case of chlorine we found the density to be 0.00316; what space do 35.45 g. of chlorine occupy? Be sure you make no mistake. What does the density mean?

P. The density is equal to the weight of one unit of volume, and the unit of volume is one cubic centimeter.

M. Yes. So 1 ccm. of chlorine weighs 0.00316 g.

P. Aha; now I see. It follows that 1 litre of chlorine weighs 3.16 g., or 3.16 g. of chlorine occupy the space of 1 litre, and 35.45 g. of chlorine the space of 35.45/3.16 = 11.2 litres.—It comes out exactly the same number! That is remarkable!

M. So, what does this imply?

P. That 1.01 g. of hydrogen and 35.45 g. of chlorine occupy the same volume.

M. Not only this, but that equal volumes of hydrogen and chlorine unite to form hydrogen chloride. Now this has the density 0.001625; so what space is occupied by 36.46 g. of hydrogen chloride, which consists of 1.01 g. of hydrogen and 35.45 g. of chlorine?

P. 36.46/1.625 = 22.4 litres.

M. Does nothing strike you here? Just compare this with the former numbers.

P. It is exactly double. But this must be some joke!

M. It is no joke, but earnest. Here, again, you see the first example of an important law of nature.

P. Another one! I am always meeting with a law of nature without knowing it. Does this happen to everyone?

M. You should answer that yourself. I purposely guide

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you so that you have to knock against the laws of nature which I wish to make known to you.

P. Just so; it is, therefore, no chance meeting.

M. Now, try to express in a general manner what you have just seen.

P. If chlorine and hydrogen combine, the volumes are equal.

M. Better; chlorine and hydrogen combine in equal volumes. And the hydrogen chloride—?

P. Has double the volume.

M. Right. And all other combinations behave similarly.

P. Is that really the case?

M. Yes; only the volumes are not always equal, but as 1:2, 1:3, 2:3, etc. We can represent the volumetric proportions of the gases that enter into combustion with each other by the term $m:n$, where m and n are quite small numbers.

P. So it is the same as in the case of the combining weights!

M. Yes; and the volumes of the resulting compounds are also in a similar, simple proportion to the volumes of the constituents. I give here the gaseous densities of a number of substances, of which you already know; just calculate out what volume, in litres, one combining weight of each substance would occupy.

	Densities.
Oxygen.	0.00143
Hydrogen.	0.0000901
Water	0.000804
Nitrogen.	0.00125
Carbon monoxide.	0.00125
Carbon dioxide.	0.00196

P. To do this I must, as before, divide the combining weight by the density multiplied by 1000.

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M. Quite right. Draw up another table.

P. Oxygen.....	16.	:1.43	=11.2
Hydrogen.....	1.008	:0.0901	=11.2
Water.....	18.02	:0.804	=22.4
Nitrogen.....	14.04	:1:25	=11.2
Carbon monoxide.....	28.	:1.25	=22.4
Carbon dioxide.....	44.	:1.96	=22.4

How wonderful! All the figures are either 11.2 or 22.4!

M. Yet you ought not to be surprised; it must be so, according to the law which you have just learned.

P. How so? I learned that in any one compound the gaseous volumes were present in simple proportions; but yet it does not follow from this that all combining weights have equal volumes.

M. But, of course, that follows. Think; let us start with chlorine: 1 litre of chlorine unites with 1 litre of hydrogen. But, now, the hydrogen, as well as the chlorine, can form other compounds, with, for example, oxygen. Here, likewise, the law has force: 1 litre of hydrogen can only unite with 1 (or else some simple multiple of 1) litre of oxygen. And thus it continues; so, if you start with one complete litre of a gas, all other gases of elements or compounds, which react with it, whether in combination, decomposition, or any chemical process whatsoever, must always be maintained in complete litres. And the same holds good if your unit is not 1 litre, but 11.2 litres.

P. I understand, now; it is quite similar to the case of the combining weights.

M. Quite right. So, what is the relationship between the density and the combining weight?

P. Let me think. The densities of different gases are the weights of 1 ccm., and so of equal volumes; equal volumes unite—yes, so then the densities must be proportionate to the combining weights.

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M. Quite right. I hardly expected you would make it out the first time.

P. I am now bolder in expressing a law of nature.

M. Well, that is an important step in advance. However, what you said was not quite complete; sometimes the factor 2 appears. The combining weight of hydrogen is 11.2, but that of water is 22.4, times as great as the gaseous, i.e., vapour, density.

P. Yes, that is somewhat confusing. How does it happen? Can we not choose the combining weights so that everything will agree?

M. No, that would not coincide with the volumetric proportions established by fact. Think of the case with which we started: 1 part by volume of chlorine and 1 part by volume of hydrogen give 2 parts by volume of hydrogen chloride. If the densities were in a simple proportion to the combining weights, the hydrogen chloride would have to occupy one part by volume, and not two. But, then, it does not; thus we can, by no way, choose the combining weights so that they will stand in a simple proportion to the gas densities.

P. That is a pity, it would have been so convenient!

M. So chemists thought, and therefore they provided a new idea, the molecular weight. This represents the weight of 22.4 litres of the substance in a state of gas.

P. So that is generally the same as the combining weight.

M. Look in the table: when is it the same, and when is it different?

P. I think I have discovered another law of nature; in the case of compounds it is the same, with elements it is different.

M. That, to be sure, is the case here; but it is not always so.—Now, how must the formulæ of the elements be written so that they may represent one molecular weight, or 22.4 litres?

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P. If I understand your question correctly, the formula must be doubled in all cases where the old formula represents only 11.2 litres.

M. Very good; you have understood what I meant.—Formulæ which represent one molecular weight we call molecular formulæ; so write down for me the molecular formulæ of hydrogen, and of chlorine.

P. 2H and 2Cl.

M. No; we do not write it that way, but H_2 and Cl_2.—Now write the equation for the formation of hydrogen chloride from its elements.

P. $H_2 + Cl_2 = H_2Cl_2$.

M. That, again, is not correct. The molecular formula of hydrogen chloride is the same as the ordinary formula, because 36.46 g. have a volume of 22.4 litres; so you must write

$$H_2 + Cl_2 = 2HCl.$$

P. Yes, I understand. But what is the use of this?

M. The equation now shows you the proportions of the reaction not only by weight, but also by volume. For, since the molecular formulæ are chosen so as to represent equal volumes of the different gases, the figures which stand in the equation before the individual formulæ express also the number of the units of volume which are assigned to them. You can read the equation thus: 1 part by volume of hydrogen gas and 1 part by volume of chlorine gas give 2 parts by volume of hydrogen chloride gas.

P. Yes; now I see; by using molecular formulæ in an equation we can say something more than with the ordinary formulæ. But how do we discover how to write molecular formulæ?

M. The formulæ of elements are very often doubled; this is the case, for example, in the above instance where we have Cl_2, not 2Cl. In other cases, we always write mole-

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cular formulæ, when possible; but other than the above, there is no general sign in use to show that such are intended.

P. Then, why do we not always write molecular formulæ?

M. Because only a portion of all the known substances is in a state of gas or vapour. You ought not to forget that the conception of the molecular weight is based on a knowledge of the gas or vapour density.

P. Yes; that brings me to another question which has lain on my memory.—The density of a gas is, I know, variable, and, like the volume, alters with the temperature and pressure: then, how can such a simple law hold good for these variable quantities?

M. You have forgotten what I told you about the rules which have to be considered in expressing gaseous densities; we state the densities at the pressure of one atmosphere and at the temperature of melting ice, or 0° C.

P. Pardon me; I remember now. But what if a gas, such as water-vapour, becomes under these conditions a liquid, or a solid?

M. Then we just compare the volumes at some suitable pressure and temperature.

P. I do not understand!

M. You know that all gases change in volume to an equal degree, if we vary the pressure or temperature. Thus, if the quantities of chlorine and hydrogen, which unite to form hydrogen chloride, occupy at 0° and 1 atmosphere's pressure corresponding volumes, they also occupy at 300° and 1/10 atmosphere's pressure corresponding (even if other) volumes; and the same holds good at every other temperature and every other pressure, only supposing that both gases are compared at the same temperature and the same pressure.

P. Yes; I had not thought of that. But I must admit that I have not yet quite so clear a view of the subject as to be convinced that, once again, it is much simpler than I supposed.

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M. Well then, let us consider the question from another point. The law can be expressed in the following terms: if we take of whatever substances we please (supposing that they can be vaporized) as many grams as the molecular weight has units and convert them all into gases at the same temperature and pressure, they will all occupy the same volume.

P. That looks like a new law!

M. No; it is the old one. If we take the ordinary combining weights, instead of the molecular weights, most of the substances (namely the compounds) will occupy equal volumes; but some (namely the elements) will have only $\frac{1}{2}$, often, indeed, only $\frac{1}{4}$, $\frac{1}{6}$, or $\frac{1}{8}$ of the volume.

P. Please show me how this law agrees with the old one.

M. It is very simple. Chemical processes only take place in the proportion of the combining weights (or their multiples), and the combining weights yield gaseous volumes which are equal (or of simple proportions); so the chemical reactions of gases take place only in simple proportions by volume.

P. Hurrah, now I have grasped it. So, again, it is quite a simple matter.

M. Yes; it is simple. But it was not sufficiently plain to chemists, so they brought it into association with the atomic theory. At first the following conclusion was made: since the densities of the gaseous elements are in proportion to their atomic weights, an equal number of atoms are present in equal volumes of the different gases.

P. That appears to be somewhat too hasty a conclusion.

M. It is, in a sense, quite correct. The densities are equal to the weights of equal volumes. Thus, if the weights of 1 ccm. of hydrogen and chlorine are as 1.01 : 35.45, and the weights of one atom of hydrogen and chlorine are also as 1.01 : 35.45, there must be in 1 ccm. of hydrogen just as many atoms as in 1 ccm. of chlorine, for, otherwise, this equal proportion of weights would not exist.

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P. Yes; now I understand.

M. But that does not agree in the case of compounds; for the densities of hydrogen and hydrogen chloride are not as 1.01 : 36.46, but as 2.02 : 36.46. The difficulty is the same as the one we considered above. (P. 61.)

P. Yes; then how did they get over it?

M. Exactly in the same way as I described to you before. They assumed that the atoms of elementary substances combine with one another in pairs, or larger numbers, and form compounds of the same kind of atoms; just as in the case of compound substances groups are formed of different kinds of atoms. These compounds we call molecules, and from this comes the designation molecular weight.

P. What purpose does this serve?

M. We can now say: equal volumes of whatever gases or vapours you please contain equal numbers of molecules of their respective substances (supposing the pressure and temperature to be constant).

P. This seems to me to be just like the case of the atomic theory; it does not teach us more than we already know.

M. You are quite right; but for many it is a convenient aid to memory. Also it has proved a very convenient and useful means of enabling us to express the mutual relations and changes of the different substances, by selecting formulæ capable of corresponding to the volume of 22.4 litres (measured under normal conditions). Therefore the molecular theory has obtained nearly as great an importance and acceptance as the atomic theory, in which the whole of present day chemistry is, in a sense, bound up and represented.

P. But yet the theory is not necessary.

M. It is not; but even if we wished to desist from using it for its own sake, we must still employ it as a means of expressing ourselves intelligibly to other chemists.

P. But you yourself told me that only a moderately small

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portion of the known substances is found in the state of gas or vapour.

M. Quite so; but we have found that laws, similar to the laws of gases, are admissible for dissolved (instead of gaseous) substances, and by these means we can apply the idea of the molecular weight to nearly all substances.

P. Please tell me how you do this!

M. I cannot describe it to you for a long time yet; you must first become acquainted with a number of other substances, so as to know how to apply these new laws.

9. ELECTROLYSIS.

M. Can you mention, briefly, what you learned yesterday?

P. I thought you would ask me that, and I think I can tell you quite briefly: the combining weights of gases occupy equal volumes.

M. That is pretty good, only instead of combining weights you must say molecular weights, and add that they are either equal to, or multiples of, the combining weights.

P. Then is a molecular weight never a fraction of the combining weight?

M. No; for we have chosen the volume 22.4 litres just so that no fractions can occur. If we had chosen 11.2 litres we would have had to provide nearly all the formulæ of the compounds with the factor $^1/_2$, in order for them to represent this volume.

P. But we could also have chosen 44.8 or 67.2 litres?

M. Certainly; but then all the molecular formulæ would have to have the common factor 2, or else 3. That would cause useless confusion.

P. Quite so; now, my mind is at ease about everything which had seemed out of order.

M. You have, so far, been taught only the simplest instances where two gases combine in equal volumes. We will now have to do with somewhat more complicated cases. Just

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calculate for me the volumetric proportions from the following densities which have been found by experiment:

		Densities.
	Hydrogen	0.000090
	Oxygen	0.00143
	Water-vapour	0.000804
P.	Hydrogen gives	1.01/0.090 = 11.2 litres
	Oxygen	16.00/1.43 = 11.2 litres
	Water-vapour	18.02/0.804 = 22.4 litres

So there are equal volumes of hydrogen and oxygen and double as great a volume of water-vapour. This is just as was the case with hydrogen chloride.

M. You are wrong. What is the formula for water and the chemical equation for its formation from its elements?

P. $2H+O=H_2O$.

M. Yes. Now you know already that hydrogen has the molecular formula H_2, because one combining weight only occupies the space of 11.2 litres. How is it with oxygen? Look at your own calculation!

P. 16.00 g. of oxygen have a volume of 11.2 litres; so we will have to write O_2 also in order to obtain 22.4 litres.

M. Very good; and the water-vapour?

P. It already has its 22.4 litres, so it does not need to be again doubled.

M. Now, write the equation for the formation of water once more with the molecular formulæ.

P. Let me think, H_2+O_2.—No, that won't do. Aha! so it will be $2H_2+O_2=2\ H_2O$.

M. Quite right. And how do you express that in volumes?

P. Two volumes of hydrogen and one volume of oxygen give two volumes of water-vapour.

M. Bravo! You are in unusually good form to-day.

P. I must confess I read this a short time ago in a book.

M. Quite right, as long as you know and understand it.

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P. I really only understood it now. And I must say I wish very much that I could discover these things, not only by calculation, but directly on seeing them.

M. We'll soon remedy that. Let us decompose some water and collect both the constituents.

P. How will you do that? Don't we always make the oxygen combine with something in order to set free the hydrogen?

M. I will do it with the electric current. If we pass this through some solution of a salt, an acid, or a base, they separate into their constituents.

P. How does that happen?

M. I can only tell you the particulars later on. To begin with, you know that the electric current can do work.

P. Yes; it drives the electric street-cars.

M. It can also produce other work, for example, the light and heat in the electric lamp.

P. Yes, that is true.

M. It can also do chemical work by separating the elements from their compounds.

P. Now I begin to understand! We can take for our purpose the current used in the electric lamps?

M. Yes; but we must leave the lamp connected, else the current would be too strong. I sever one of the two covered wires which connect the plug with the lamp; free the ends from the insulating covering; and join each to a piece of bright iron wire by wrapping it round them (Fig. 9). The iron wires are stuck through the cork of this small piece of apparatus (Fig. 8), which consists of an inverted jar with the bottom broken off.

P. Did you make that yourself?

M. It is not difficult. You just make a scratch with the glass-cutter (I. p. 74) where you wish the crack to be, and then you bind round two pads of wet paper so that they are 0.3 to 0.5 cm. from each other, with the scratch in between.

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Now, if you give the jar a turning motion over a flame, so that the space between the two pads become heated, after some time the glass will crack off exactly along this line.

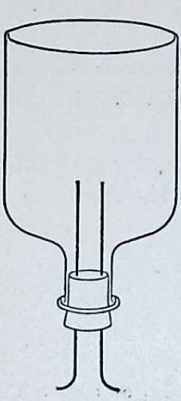

FIG. 8.

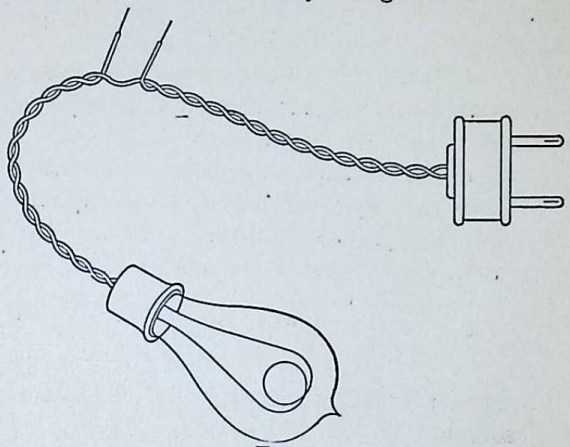

FIG. 9.

P. Why?

M. I have already told you (I. p. 20) that unevenly heated glass cracks on account of the tension set up. By means of the wet pads the heat is confined to the line in between them, and the scratch makes the glass crack easier. Only you must remove the sharp edges by going over them with a file.

P. I'll try my hand at this by and by.

M. Now I pour a solution of sodium hydrate into the glass, and make the contact: you see, bubbles of gas immediately form at both the wires, and rise up.

P. That is wonderful! Please explain it to me.

M. Of what does sodium hydrate consist?

P. Of sodium, oxygen, and hydrogen. It has the formula NaOH.

M. Right. And the electric current decomposes it, so that the sodium separates out at one wire, the hydroxyl at the other.

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P. But I see neither the one nor the other.

M. Sodium acts on water, as you know, and forms—

P. Hydrogen and sodium hydrate. The equation is

$$Na + H_2O = NaOH + H.$$

M. Good. You see it is the hydrogen of the water which evolves, and sodium hydrate is always being reformed.

P. But the hydroxyl?

M. This, also, cannot exist by itself; it splits up into water and oxygen, according to the equation $2OH = H_2O + O$. If $2OH$ separates out at the one wire, then $2Na$ must appear at the other; and you have simultaneously

$$2Na + 2H_2O = 2NaOH + 2H,$$
$$2OH = H_2O + O.$$

On the left-hand side you have elements to represent two sodium hydrate and two water; on the right you again find two sodium hydrate, but only one water. The other combining weight of water is split up into hydrogen and oxygen.

P. Please let me go over that once again. Right; that is the case.

M. Thus the current has decomposed the original sodium hydrate; but by other reactions, fresh sodium hydrate has been formed again, and only the water has been broken up. Therefore we can look on the whole process as a decomposition of the water.

P. I would not have dared to twist the formulæ round like this!

M. They are quite correct; of course it was a long time before we understood the subject correctly. But now, let us leave all these details on one side and confine ourselves to the fact that, in the end, only the water is decomposed. One of the gases which rise up from the wires is oxygen, and the other is hydrogen; both appear in the same proportion as they form water, namely, $2H$ to $1O$.

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P. Can I see that?

M. Yes; let us collect the gases. To do so, we take tubes, like burettes, only with the pinch-cock uppermost; dip the open end into the liquid, and fill them by suction, first keeping the pinch-cock open and then closing it at the proper time, so as not to get any of the liquid into the mouth.

P. Is it poisonous?

M. Not exactly; but it is corrosive and very disagreeable to the taste. Now both the tubes are arranged so that each takes in one of the gases. You very soon see that much more gas collects in the one than in the other.

P. Then the greater quantity will be the hydrogen?

M. Quite right, and the oxygen is in the other tube.

P. Both gases appear exactly the same!

M. We will soon distinguish between them. In order to remove the two tubes full of gases securely, I have here a cone-shaped cork fastened on to a strong bent wire; with this I can close the tube under the liquid (Fig. 10) and transfer it to another vessel.

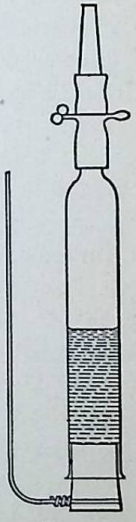

FIG. 10.

P. I was wondering the whole time how you would do this; it never occurred to me that it was so simple!

M. I now place both tubes in a large vessel of water; and you can easily tell by the eye, that in one there is about double as much gas as in the other.

P. Can we not measure this more accurately?

M. To be sure; but that would take more time and trouble than we can spend. We have made these measurements accurately and the proportion is very nearly, but, yet, not quite as 2:1.

P. Then how do you account for that?

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M. The laws of gases are not quite rigid. (I. p. 208.) The proportion of 2:1 becomes more exact as we diminish the pressure. But as we increase the pressure, the oxygen decreases in volume quicker than the hydrogen; and, therefore, we find for two of hydrogen less and less than one of oxygen; yet, after all, the difference is only very small.

P. Now we will set a light to the hydrogen!

M. Quite right; I sink the tube up to the pinch-cock in water, hold a burning match at the outlet, and open the cock—

P. It burns!

M. With the characteristic pale flame.

P. And the oxygen?

M. We treat it in the same way, and allow the gas to play on a glowing match.

P. Hurrah; this burns also!

M. So you see the tests have answered.

P. I would like to do the whole experiment over again for myself; but we have no electric light at home.

M. Then see if you can not obtain three galvanic cells, or better still, two charged accumulators. You must always connect the opposite poles and fasten the iron wires to the first and last pole. But it will be better for you to postpone the experiment until you have learned to work with the galvanic battery.

P. But then, tell me, can we also decompose other substances in this way,—perhaps hydrocholric acid? This would produce equal volumes of hydrogen and chlorine.

M. Quite right; but it is a difficult experiment to arrange; because the chlorine does not evolve as a gas, but is dissolved in the hydrochloric acid. A large quantity of chlorine is required to saturate the hydrochloric acid. In other respects, it is a pity that we cannot make this experiment in the same way as with the water; for the hydrogen chloride is decomposed directly into its elements, chlorine and hy-

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drogen, without any side reactions. Only we dare not use iron wires to lead the current into the hydrochloric acid, because they would become dissolved.

P. Then what do we use?

M. The artificially-prepared carbon sticks, such as are used in the electric arc-lamps are the best.

P. I would like to know and see something more of electricity.

M. I can mention one or two points. You know that it is associated with a kind of energy which can be obtained from work (put into the dynamo and also the ordinary electric-machine) which in this way, can be changed into various other kinds of energy.

P. Yes; you have already told me that.

M. Very well. The most important variety of this energy we call the electric current which passes through the conductors.

P. Then what is it that flows along in this current?

M. The electric substance or, as we say for short, the electricity.

P. But we see nothing on the wire!

M. If I let water flow through a glass tube you see nothing. You only see something if a bubble of air or another foreign substance gets inside. And, in the same way, you cannot perceive the flow of a river except by the unfamiliar objects born on the current.

P. Yes; that is true. I never thought of that.

M. Well, in the same way as flowing water can do work so can the electric current. The amount of the work depends on the quantity of electricity, and also on the pressure with which the current is drvien. The unit for this pressure is called a volt. The unit for the quantity of electricity is called a coulomb, and the work of a current is expressed by the product of the volts and the coulombs. There are instruments which measure both.

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P. Yes; I have just had an electric installation shown to me by a friend. It belongs to his father. On the switch-board were things like clocks; volt was written on some, but I did not see coulomb.

M. But you saw ampère?

P. Yes; that was the name.

M. This means that we won't know at all what quantity of electricity is passed by the current, only the time during which it passes. A large stream and a small rivulet could pass the same quantity of water, if we let the stream flow a short time and the rivulet a long time; any difference just depends on how much water both pass in the same time.

P. I see that.

M. We have, therefore, introduced a special gauge for the quantity of current during a unit of time, and that we call an ampère. An ampère is a current which passes one coulomb in one second.

P. I understand this, but I fear I will confuse the names.

M. Write down this table:

Unit of electric quantity =coulomb.
" " strength of current=ampère=$\frac{\text{coulomb}}{\text{second}}$.
" " pressure =volt.

P. I don't think I will be long in learning that.

M. Now we can compel the current to do chemical work, if we lead it through a solution of a salt.

P. How can we compel it? Can it not simply pass through as through a wire?

M. No; that's just what it can not do. It is as if you were to lead a current of water into the lade of a water-wheel or a turbine. If it goes through at all, it must set the wheel in motion.

P. And what sets the electric current in motion?

M. The constituents of the salt. This is the difference

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between the electric current and the water current; the latter only goes in one direction, but the electric current is a double stream in which the positive quantities of electricity flow one way, and the negative in the opposite direction.

P. I can perhaps imagine, but could not express this. Then how is it possible for the two kinds of electricity to flow in opposite directions in the wire without interrupting each other!

M. You can make this quite clear to yourself. If you produce waves simultaneously, at two points on a quiet pond, they pass, in opposite directions, through each other without causing any interruption.

P. Yes; that is true.

M. Or take the case of a band which transfers work from one machine to another. One half of the band is always travelling in the one, the other half in the opposite direction. If two bands are enclosed within a small case they afford quite a good idea of the electric current.

P. I see. But all these are only suppositions and comparisons.

M. We cannot have any closer perception than this, because we have no faculties which enable us to observe the electric substance directly. But as we can calculate, quite accurately and correctly, electrical effects, we do not need the suppositions.—Now, I told you that the constituents of the salt are moved in opposite directions by the electric current; the metals go in the direction of the positive electricity; chlorine, or the other corresponding elements or compounds, pass in the opposite direction.

P. Please make that a little clearer.

M. Imagine a number of boys and girls all together: that is the solution. Then the boys are called from one side, the girls from the other: that is the effect of the current. The boys run to one side, the girls to the other; and so the become separated.

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P. And the boys are the metals, and the girls the other constituents?

M. Whichever you prefer. Since the metals go with the positive current, we call them the positive constituents of the salt; and the others, the negative. We also call the former cathions; the latter, anions.

P. Then, what does that mean?

M. Ion denotes a traveller, and the prefixes cath- and an- imply downwards and upwards. The positive constituents travel with the current, down-stream, the negative travel against the current, up-stream. The words are taken from the Greek.

P. Well, that was not actually what I wished to hear from you; I was thinking of machines and things of that kind. But what you said was also very interesting.

M. I will conclude by giving you some names. Chemical decomposition by the electric current is called electrolysis, and the substances thus decomposed are electrolytes. The cathions and the anions are both called ions. Each electrolyte consists of ions, cathions, and anions. Decomposition ensues when the ions collect at the two conductors which lead the current into the electrolyte. We call these conductors electrodes; that conductor at which the cathions separate out is the cathode; and the anode is that at which the anions appear. I have written down these names here for you; learn them by heart for next time.

P. I believe I know them by heart already.

10. ACIDS.

M. I assume that you have learned the names I gave you; but what of yesterday's lesson?

P. I think I understood it very well. In electrolytes, the cathions travel with the positive, the anions with the negative, electric current. They are, respectively, carried off

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and separated at the points where the current leaves, and where it enters, the electrolyte. These points we call electrodes.

M. Very good; but now, if you think of what happened during the electrolysis of the sodium hydrate, you will perceive that we do not always obtain a sight of the ions at the electrodes; sometimes they are changed by some chemical reaction, because they cannot withstand the prevailing conditions.

P. On what does this depend?

M. Just on the conditions. Such substances, for example, as react chemically with water, naturally cannot exist in the presence of water; and such ions as OH, which cannot remain in the free state after their separation, become changed into other stable substances. By applying these rules, we can come to understand most cases.

P. I am not yet very clear about this.

M. That is very natural; just wait, we will soon have another example, and then you will understand the circumstances better.

P. It is with chemistry just as with a new house: we have seen over everything, but still we do not yet exactly know where everything is, and where every door leads to.

M. Quite right; but I think you will soon become more and more at home.

P. Yes; for we really always keep to the same room.

M. You mean that we always start again from hydrochloric acid? This room has many doors into other apartments, so that is why we use it most. We will now quickly glance over another room, called sulphuric acid.

P. I have already seen this. (P. 28.)

M. Yes; as a dilute solution in water. Do you remember its chemical formula?

P. I do not know it by heart, but I won't be long in looking it up; I will obtain it that way. The formula is H_2SO_4.

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M. What does it mean?

P. That sulphuric acid consists of two combining weights of hydrogen, one of sulphur, and four of oxygen.

M. And the proportions by weight?

P. I must look for these in the table, (P. 38.) We have:

hydrogen	2.02
sulphur	32.06
oxygen	64.00

M. Right. A substance of very nearly the same composition as this is in this flask.

P. It looks like water!

M. Just take the flask in your hand and shake it gently.

P. O! It is much heavier than water, and it moves more slowly, just like oil.

M. Quite right. Sulphuric acid has the density 1.85; so it is nearly twice as heavy as water, and also has a much greater viscosity.—I pour some into a flask of water: just touch the outside of the flask.

P. It has become quite hot.

M. Yes; if sulphuric acid is mixed with water a large quantity of heat is produced.

P. Then where does it come from?

M. Chemical reactions take place between sulphuric acid and water, you will learn more about these later on, and heat is caused thereby. You can also express this in these words: sulphuric acid and water contain a greater quantity of energy when separate than after intermixture; this greater quantity appears as heat.

P. So it is just the same as in the case of combustion, where substances contain more energy before entering into combination than after.

M. Quite right. And so it happens that sulphuric acid absorbs water wherever it can. If, for example, we let it

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stand exposed to the air in a dish, it absorbs water-vapour, becomes diluted, and makes the air dryer. Therefore, in winter, we sometimes place dishes of sulphuric acid near the windows, so that no frost-wreaths can form on them.

P. You mean that if there is no moisture in the air no ice can be deposited on the cold window.

M. Very good; that's just what I mean. Only we must remember that sulphuric acid increases greatly in volume by absorbing water; we ought, therefore, to fill the dish only one quarter full, else the acid runs over and makes a bad stain.

P. Why is that?

M. Well, sulphuric acid is a strong acid: it combines with bases and decomposes salts. We will very soon enter on this subject.—Besides, its prevailing tendency makes it unite with water. I place a drop of the acid on a board: you see that very soon a black stain appears.

P. The wood looks as if it were charred.

M. Something similar has occurred. Wood consists of carbon, hydrogen, and oxygen; and, indeed, the latter are present in the same proportion as in water. The sulphuric acid removes these constituents in the form of water, and the carbon remains behind.—Even dilute sulphuric acid has a destructive effect; if a drop falls on paper it partially dries up, and the residue penetrates slowly further into the paper and converts it into an easily friable mass.

P. That is the reason why an old chemistry book, which I received from a friend, keeps falling to pieces in several places.

M. You can prove this by dabbing these places with litmus solution, or by pressing on them a damp piece of blue litmus paper.

P. I'll try that! Yes, it becomes red.

M. That shows that an acid is there. Since all acids have not this destructive effect, sulphuric acid is probably the

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cause. So you see, you must be cautious in working with this substance. Nearly all young chemists ruin their books with sulphuric acid.

P. Is there no remedy after the thing is done?

M. There is a very simple one. You only require to convert the sulphuric acid into another compound which has no corroding action.

P. Yes, but which?

M. Any salt will do. Salts do not corrode.

P. Then I will neutralize the places with sodium hydrate.

M. Pretty good, but not quite. If you moisten the places with caustic soda solution, the acid enters into combination; but an excess of sodium hydrate will remain over, and this also has a corroding effect.

P. Then I know no remedy.

M. Use sodium acetate. This forms sodium sulphate with sulphuric acid, and acetic acid is set free. This has no effect on paper, for it soon evaporates because it is volatile.

P. I don't understand that; please explain it more fully.

M. This will be most easily done by means of one or two formulæ. Acetic acid is, like all acids, a compound of hydrogen; let us denote it by HA, where A represents the elements which are associated with the hydrogen. Then the sodium salt of acetic acid has the formula NaA. Why?

P. Because, when a salt is formed from an acid the hydrogen is replaced by the metal. (P. 15.)

M. Good. Now I let hydrocholric acid act on it.

P. Why not sulphuric acid?

M. It goes more simply with hydrochloric acid. We will deal with the sulphuric acid later on. We then have the equation

$$NaA+HCl=NaCl+HA.$$

Express this in words.

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P. Sodium acetate and hydrogen chloride give sodium chloride and . . . acetic acid.

M. Right. That teaches us this general rule: in order to obtain an acid from its salt you must decompose it with some other acid.

P. Then we must be able to make hydrochloric acid from sodium chloride and acetic acid?

M. You have put a very difficult question. Chemists have worried their heads about this since the earliest times. On the whole, you are right: every acid decomposes, in the above sense, every salt. But the amount of acid which is formed is very different, according to circumstances.

P. I thought that as much was formed as the chemical equation shows.

M. No; so much is never formed all at once. On the contrary, all the four substances, which appear in the equation, are present nearly the whole time. But if one of the substances is volatile, as the acetic acid is in this case, it goes away, and there remains behind the substance which stands next to it on the same side of the equation, in this case the sodium chloride.

P. I think I have understood; but I feel that I have still much to ask you.

M. That is, no doubt, because there is still very much to say on this subject. But, in the meanwhile, we will be satisfied with what has been said.

P. Please just tell me whether the sulphuric acid acts in another way.

M. Only as far as external appearances go. Sulphuric acid contains two combining weights of hydrogen, which can be replaced by metals, and therefore acts on two combining weights of sodium acetate. The equation is

$$H_2SO_4 + 2NaA = Na_2SO_4 + 2HA.$$

P. So there is really no great difference.—But I have kept

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you too long with my questions about the sulphuric acid stains on my old book—

M. We have just come to the point which I wished to enforce. What we discussed gives us an idea of how to prepare hydrochloric acid. Just write the equation for the action of sulphuric acid on sodium chloride.

P. H_2SO_4+NaCl. . . .

M. Remember that sulphuric acid contains two combining weights of hydrogen.

P. Yes; so it does. Then:

$$H_2SO_4+2NaCl=Na_2SO_4+2HCl.$$

M. Express this in words.

P. Sulphuric acid and sodium chloride give sodium sulphate and hydrogen chloride.

M. Right. Hydrochloric acid is prepared by this process on the large scale.

P. How is the sulphuric acid got?

M. We make it by burning sulphur.

P. Can't we do the opposite and decompose sodium sulphate with hydrochloric acid?.

M. Yes; using a solution in water.—But if we take sulphuric acid containing no water, or only a little, the hydrogen chloride is evolved as a gas, and we can make the decomposition complete.

P. I don't understand that: we can only drive off as much hydrochloric acid as is formed, and that, as you said before, is only a portion.

M. Your reasoning is good. The fact is that a kind of equilibrium is set up between the four different substances, which depends on the quantities present. If a portion of the hydrogen chloride escapes the equilibrium is destroyed, and the substances act on one another so that fresh hydrogen chloride is formed. This also escapes, and the process is repeated so long as sulphuric acid and sodium chloride are still present.

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P. And so the decomposition is complete?

M. Yes; that would be so, had we taken both substances in the correct proportions. Just calculate these out for me.

P.

$H_2 = 2.02$	$Na = 23.05$
$S = 32.06$	$Cl = 35.45$
$O_4 = 64.00$	$NaCl = 58.50$
$H_2SO_4 = 98.08$	$2NaCl = 117.00$

M. Right. If we take another proportion, then the substance, which is in excess, remains over.—But now, let us have deeds; of words we have had enough. We will interpret these written rules into actual experiments. Do you know the smell of acetic acid?

P. Is it the same as vinegar?

M. Pretty much. Vinegar is acetic acid dissolved in a large quantity of water, what we would call for short dilute acetic acid.

P Then I know what it smells like.

M. Very well. Here is some dilute sulphuric acid; smell it; it has no smell. This white salt is sodium acetate. I shake some into the sulphuric acid and warm it. Just smell it.

P. Yes; it smells like vinegar.

M. Let us repeat the experiment, on a somewhat larger scale, by distilling (I. p. 155, Fig. 31) a somewhat larger quantity of the mixture in a flask. The water-clear liquid, which collects in the receiver, is dilute acetic acid.

P. How can we recognize it?

M. For the present the smell and the taste must be sufficient tests for you. Now we will make hydrogen chloride; this requires rather more preparation. We place some sodium chloride in a flask, and add a mixture of five parts, by volume, of sulphuric acid and two of water.

P. Why just that quantity?

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M. No hydrogen chloride will then evolve in the cold, because it is held back by the water; on the other hand, it will come off freely on heating. We do this on a water-bath, a small boiler of enamelled iron. We lead the gas given

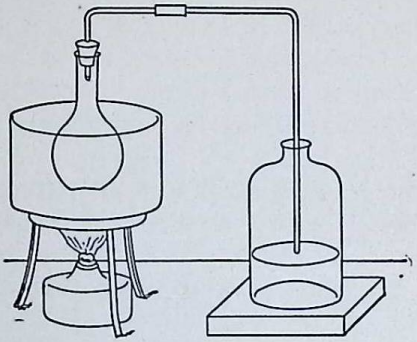

FIG. 11.

off into a jar containing water, but do not allow the tube to dip into the liquid, only come down close to the surface. (Fig. 11.)

P. Again I must ask why?

M. Hydrogen chloride gas is absorbed by water very rapidly and eagerly, and there is a risk that the water will run back into the flask if the tube is touching and the evolution of gas should accidentally cease.

P. I do not quite understand this.

M. Just think; if the apparatus is full of pure hydrogen chloride and the tube dips into the water, then the water would absorb the hydrogen chloride; on this the pressure inside diminishes, and the outside pressure of the air drives the water into the flask. There, more hydrogen chloride becomes dissolved, the pressure diminishes further; and soon all the water is driven into the flask.

P. Yes; that's what would happen. But look! Hydro-

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gen chloride vapour is now coming out of the jar, because it has not been dissolved by the water.

M. That is only a mist which disappears as soon as the air is driven out of the apparatus.—There is another peculiarity about this: when water absorbs hydrogen chloride it becomes heavier and sinks to the bottom; therefore the more dilute solution, which absorbs the gas best, is always at the surface where the gas enters.—Now, just feel the jar.

P. It is quite warm. Is that due to the hot hydrogen chloride gas?

M. No; even if cold it would form a hot solution. A great quantity of heat is set free by the solution of hydrogen chloride in water.

P. Is this the same as is the case with sulphuric acid? (P. 78.)

M. Partly; but a portion of the heat is also due to the fact that the hydrogen chloride changes from its gaseous condition.

P. And the liquid produced is ordinary hydrochloric acid?

M. Yes. Now we will make the experiment which I

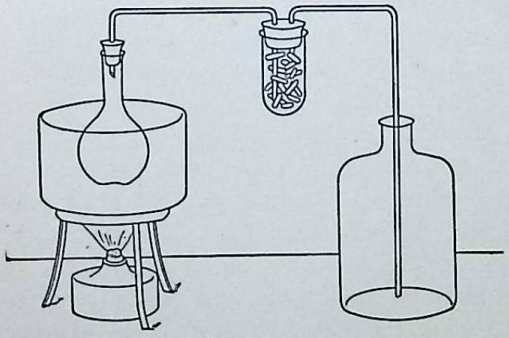

FIG. 12.

promised you before. (P. 50.) There is sodium hydrate in this glass; I lead hydrochloric acid through a tube into

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it; the exit tube dips into an empty jar. You see that water-vapour is very soon formed. It condenses to water in the jar. (Fig. 12.) Express your thanks by writing down the equation for this reaction.

P. $NaOH + HCl = NaCl + H_2O$.

M. Right!

11. SALTS.

M. Rehearse!

P. I learned yesterday how to make hydrochloric and other acids: we heat their salts with sulphuric acid.

M. You have expressed this rather too concisely; to be sure, we generally use sulphuric acid, but for what reason?

P. Perhaps, because it is cheapest.

M. That would be one advantage, but it is not the decisive reason. What property must the acid which we produce have?

P. I know of no special one. We simply apply heat and the acid comes off as vapour, or gas, and can be collected.

M. You have described just the property I want: the acid which we wish to obtain must be easily volatile, and the acid which we use for the decomposition of the salt must be non-volatile. Sulphuric acid has this latter property, and, therefore, we use it for this purpose.

P. Then, conversely, can we not also decompose sodium sulphate with hydrochloric acid?

M. You have asked me that already, and I told you that in the liquid condition a partial reaction takes place. But if we apply heat the hydrochloric acid just evaporates away and the sodium sulphate remains behind, as if it had never been decomposed at all.

P. Ah; I now, for the first time, understand this. It is just what you described on p. 82. So sulphuric acid is not easily volatile?

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M. No; it only boils at 338° C.; while the highest boiling mixture of water and hydrochloric acid boils at 110°, and water-free hydrogen chloride is a gas.

P. And what of acetic acid?

M. It boils at 118°, so it is out of the question. Now let us learn another, and last, law about hydrochloric acid, and then we can leave it for some time. What are the salts of hydrochloric acid called?

P. The salts of hydrochloric acid? The question sounds so strange. Ah, they are the chlorides. (P. 7.)

M. Quite right. How do we obtain them?

P. By replacing the hydrogen of the acid with a metal.

M. Right. I have here four glasses, each containing 5 g. of hydrochloric acid; I throw into one some iron nails, into another some slices of zinc-plate, into the third some magnesium, into the fourth some aluminium. In all cases hydrogen evolves; and you must here take care that the maximum quantity of each metal dissolves.

P. How shall I do this?

M. If the metal has completely dissolved add some more until the liquid no longer acts on it.

P. All the hydrogen has then been driven off?

M. Quite right.—Now there is another method of making salts from acids.

P. Yes; with the bases.

M. Quite right; neutralize three other portions of hydrochloric acid with caustic soda, caustic potash, and calcium hydrate; you can make sure, with litmus paper, when the solutions are neutral.

P. We now have seven salts of hydrochloric acid.

M. We will make one or two more. A salt is formed if we treat an acid with the oxide of a metal, for example, mercuric oxide:

$$HgO + 2HCl = HgCl_2 + H_2O.$$

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P. That is just the same reaction as in the case of a base!

M. Not quite; with a base, water is formed from hydroxyl and hydrogen; and, therefore, in the latter case, there is twice as much water as in the former.—I will make the mercury salt myself, for it is very poisonous. I heat a little dilute hydrochloric acid, and add a small quantity of the mercuric oxide. At first it disappears, i.e., it dissolves, forming a clear solution. I will add some more, but probably little more will dissolve. All the hydrochloric acid is then saturated and changed into the mercury salt.

P. Is there still another method of preparing a salt?

M. Certainly; you know of another: by the decomposition of the salt of a volatile acid.

P. Yes. But are there acids more volatile than hydrochloric acid?

M. Certainly; for example, carbonic acid. This has the composition H_2CO_3; and its calcium salt therefore has the formula $CaCO_3$, for one combining weight of calcium can take the place of two hydrogen. (P. 48.) Ordinary chalk is calcium carbonate. If I pour hydrochloric acid over some chalk the mixture effervesces, because the carbon dioxide evolves as gas, and calcium chloride remains as a residue. If no more gas comes off then the hydrochloric acid is saturated.

P. I think it will be difficult for me to remember all this.

M. It is not so bad as you think; I will write the four methods down for you, and shall use the calcium salt in all cases as it affords a better comparison:

1. From a metal. . . . $Ca + 2HCl = CaCl_2 + 2H$.
2. From a base. . . . . $Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$.
3. From an oxide. . . $CaO + 2HCl = CaCl_2 + H_2O$.
4. From a salt. . . . . $CaCO_3 + 2HCl = CaCl_2 + H_2CO_3$.

P. Yes; it is quite easy!

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M. Let us make some copper chloride by the fourth process. We take this blue powder; it is copper carbonate; we can buy it in the colour shops as *ultramarine.* If I pour some hydrochloric acid over it it effervesces, and I obtain a green solution of copper chloride.

P. We have now plenty of chlorides!

M. You must carefully filter the solutions into clean glasses; use a fresh filter-paper each time and do not forget, also, to wash out the funnel each time!

P. I will do this as well as I can.—

M. Now we have solutions of the following metallic chlorides:

Sodium chloride	$NaCl$
Potassium chloride	KCl
Iron chloride	$FeCl_2$
Zinc chloride	$ZnCl_2$
Magnesium chloride	$MgCl_2$
Mercury chloride	$HgCl_2$
Copper chloride	$CuCl_2$
Aluminium chloride	$AlCl_3$

You see that each one combining weight of the different metals is united with one, two, or three combining weights of chlorine.

P. What is the reason of this?

M. It is a property of the elements which you must, to begin with, simply learn by heart. Later on you will come to know a rule dealing with this subject.—And now there is another fact of interest to us. Lay out eight glasses with 100 ccm. (roughly measured) of distilled water in each; and add, separately to each, some drops of the various metallic chlorides.

P. I have done so.

M. This clear liquid here is a solution of another salt,

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called silver nitrate. I let a few drops fall into each glass, and shake. What do you see?

P. In each case a white cloud gathers.

M. Yes, a white precipitate is formed. It is silver chloride.

P. So it also is a metallic chloride!

M. Quite right; but it differs from all these other ones, as it is not soluble in water.

P. Not at all?

M. We cannot say that; but it is very slightly soluble, for 1 litre of water only dissolves 0.0015 g. So if more than this is present a white precipitate is formed.

P. Look, it has become quite grey!

M. The glass was standing in the sun; the light has decomposed the silver chloride and coloured it grey.

P. How can light do this?

M. Light is also a kind of energy; so it can do chemical work, under certain conditions.—But let us return to our subject. You have seen that all the salts, which have been formed with hydrochloric acid, give with a solution of silver just the same reaction as if they all contained the same substance. This reaction is represented, in the case of sodium chloride, by the equation

$$NaCl + AgNO_3 = NaNO_3 + AgCl,$$

and the same thing always happens; namely, chloride of silver is formed if a chloride salt of any kind is treated with the silver solution.

P. Then is there something peculiar about this?

M. Yes; there are a number of other chlorides which do not exist as salts, nor dissociate as they do; they give no precipitate with silver.

P. Surely, here again, some law of nature is in the background!

M. Certainly; but I will not tell it to you yet. You must

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first make a number of other experiments which will all be comprised within this law of nature.

P. I am very fond of seeing and making experiments.

M. Well, then, repeat the experiments of the formation of the different salts, this time with sulphuric acid. Dilute the concentrated acid with twenty times its volume of water; but take care to pour the acid into the water, not the water into the acid.

P. Why?

M. Otherwise, the heat may easily increase so much that the acid will spurt out and cause damage.—

P. I have made the experiments. The metals dissolved much more slowly than in the hydrochloric acid. And with calcium hydrate and clay I could not obtain clear solutions, there was always a white substance present.

M. Calcium sulphate is very slightly soluble in water; the larger portion of the salt separates out as a solid.

P. Yes; I thought something must be happening, for the clay effervesced nearly as much as with the hydrochloric acid.

M. Now, notice. The silver solution in the previous experiment was a test for the presence of chlorine in all chloride salts. There is also a test for all sulphuric acid salts; it is called barium chloride and is the chloride of the metal barium. Barium sulphate is just as difficult to dissolve as silver chloride, and, therefore, it also forms a precipitate, which is white like silver chloride; only it is easily distinguished from the latter, as it does not turn grey in the light.

P. Shall I again dilute the various salt solutions, as before?

M. Yes; and then add barium chloride solution to all of them.

P. Right; a white precipitate forms each time. But it looks quite different from the silver chloride.

M. In what way?

P. The silver chloride collects in flocks, the barium sulphate does not.

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M. Quite right. If you give one of the glasses containing the silver chloride a good shake or stir, eventually it all forms into large flocks and the liquid above becomes quite clear. On shaking the barium sulphate it remains like a powder, as before. Therefore, this is called a powdery, and silver chloride a flocculent or curdy precipitate.

P. Why "curdy"?

M. Because it looks like curdled milk.

P. Why does it cling together?

M. We do not yet exactly know; probably because silver chloride is, in the solid condition, of a tough nature, almost like horn; while solid barium sulphate is a brittle substance. —Just write down the reaction between sodium sulphate and barium chloride; and remember that barium is equivalent to two, and also that sulphuric acid contains two, combining weights of hydrogen.

P. $Na_2SO_4 + BaCl_2 = 2NaCl + BaSO_4$.

M. Good. Just compare this equation with that for the silver chloride precipitate.

P. It appears quite similar; and, instead of sodium, some other metal can be present.

M. Right. What corresponds in this last equation to the chlorine?

P. I do not know how to name it; it is the SO_4.

M. Call it the sulphate ion; and the chlorine in the former salts, the chlorine ion.

P. What do these names mean?

M. You have, by the experiments just made, learned the law that certain constituents of the salts react in a definite manner quite independently of the other constituents. All hydrochloric acid salts, or chlorides, give the silver chloride precipitate; all sulphuric acid salts, or sulphates, give the barium sulphate precipitate. But, in the last case, it is only the SO_4 group which gives this universal reaction, never the sulphur or the oxygen alone. Therefore, these groups, which

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give these special reactions, have been provided with special names by adding ion after the class-name of the salt.

P. I do not quite understand.

M. All salts can be divided into two constituents; on the one side the metal, on the other, whatever is combined with the metal. This may be in some cases an element, for example, chlorine; in other cases, a group of elements, like SO_4. These constituents have their own special reactions.

P. Yes—you have, actually, only showed me about chlorine and SO_4. Then do the same reactions apply also to the metals?

M. Certainly. I have here the carbonic acid salt of barium, barium carbonate: this dissolves in acids in the same way as clay does. If you convert it into a salt with hydrochloric acid, nitric acid, or acetic acid, all these solutions give precipitates with sulphuric acid, or any other sulphate, in the same way as barium chloride is precipitated by a sulphate.

P. Ah! Now, I begin to believe that there really is a law of nature here. Is the same the case with silver?

M. To be sure. All solutions of any silver salt whatsoever give a precipitate with any metallic chloride whatsoever.

P. Yes; I begin to understand.

M. You see; every time a solution of a barium salt comes in contact with a solution containing SO_4 as one of its constituents, a precipitate of barium sulphate is formed, no matter what the other constituents of the salt are.

P. So, then, barium is a test for SO_4; and SO_4 is also a test for barium.

M. Excellent; I see you understand that all these tests for salts are reciprocal in effect.

P. And all that is necessary is that the two reacting substances must combine to form an insoluble salt.

M. That is also right. You are very clever in making out my meaning to-day.—Now, since these constituents of

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the salts, if they are elements, appear quite different from the elements in the so-called free state, they must also have special names.

P. Please say that once again.

M. In the solutions of the metallic chlorides you can recognize none of the properties of the free chlorine; neither the green colour, nor the smell, nor anything else peculiar to chlorine. And you see just as few traces of the metals zinc, iron, copper, etc., in these solutions.

P. That is true.

M. And yet they must be there in some definite form, for they react by themselves independently of the other constituents.

P. That is also true.

M. Therefore we must conclude that these elements are present in some condition which differs from their usual one.

P. Perhaps, the difference is similar to that between carbon and diamond?

M. In many respects, this is quite a good comparison; especially as these new forms also contain more energy than the old. But here there is another peculiarity, these forms only appear as constituents of salts. Therefore, we add the common distinguishing mark, ion, after all their names. We will express this in their formulæ by denoting all ions of the same kind as the chlorine, or as the sulphate, ion by strokes (Cl'=chlorine ion, SO_4''=sulphate ion), and all metallic ions by dots ($Na^{\cdot}$=sodium ion, $Ca^{\cdot\cdot}$=calcium ion, $Al^{\cdot\cdot\cdot}$=aluminium ion).

P. Why do you sometimes put one, sometimes more, strokes and dots?

M. You ought to know why. Just look at the table on p. 89.

P. Ah, I see; those metals which unite with one combining weight of chlorine have one dot, and so on.

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M. Right. We call these monovalent; and the others, divalent, trivalent, etc.

P. And the other ions? I mean those with the strokes.

M. Those which unite with one combining weight of sodium are, likewise, monovalent; those which unite with two, like the sulphuric ion, are divalent and have two strokes.

P. This is just the same as I learned in the case of the neutralization. (P. 47).

M. Of course; it is the same. You will soon have no difficulty in recognizing that.

P. Do these ions behave as ions during electrolysis?

M. Certainly. These are just the constituents which travel in opposite directions during electrolysis.

P. So, then, it is really only salts which can conduct the electric current and thus become decomposed?

M. Quite right; *all electrolytes are salts, and salts are the only electrolytes.* In this case, acids and bases are included; since they behave, in this special sense, just in the same way as the salts.

P. And the reactions common to all acids, for example, turning litmus red and giving off hydrogen with magnesium—

M. Are the reactions of the hydrogen ion, $H^{\cdot}$. You know that all acids are compounds of hydrogen, but all hydrogen compounds are not acids, only those which let their hydrogen change into the form of the hydrogen ion. Those reactions are thus tests for the hydrogen ion, just as the silver chloride precipitate is a test for the chlorine ion.

P. And is it the same with the bases?

M. These contain a common constituent, the hydroxyl ion, OH'; and the reactions peculiar to these are tests for the hydroxyl ion.

P. Once again, the subject is so simple that I had difficulty in realizing it.

M. I don't wonder at that; even chemists, themselves, have found it quite difficult to perceive its simplicity.

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I will show you some more experiments. I lead the electric current (p. 68) through a solution of some copper salt, whichever you please, say copper sulphate; the ends of the conductors are fitted with small pieces of platinum wire because this metal is not attacked by the substances formed. After some seconds one wire becomes covered with copper.

P. Yes; I see a red coating.

M. That is the metal. The solution contains copper sulphate, with the ions $Cu^{\cdot\cdot}$ and SO_4''; the positive electricity travels to the cathode with the copper ion, passes on through the platinum wire, and leaves the copper behind as a red metal.

P. Then we must look upon the ion as a metal in combination with electricity?

M. Such an assumption represents the facts very well, and you can stick to it. The positive ions, or cathions, are, in this sense, compounds of the metal and positive electricity; the negative ions, or anions, of negative electricity and chlorine, or SO_4, or NO_3, or whatever else may be the anion constituent.

P. Yes; then I can easily discover what becomes of the sulphate ion in this experiment.

M. It reacts with water and forms sulphuric acid and oxygen, according to the equation

$$SO_4 + H_2O = H_2SO_4 + O.$$

P. Is this similar to the case of the hydroxyl in the electrolysis of sodium hydrate (p. 70)?

M. To a certain extent, but not quite; for no water takes part in that reaction. Just consider; what will eventually become of the copper sulphate solution if we continue the electrolysis?

P. On the one hand, more copper is always being removed, and finally it will all be taken away; on the other hand,

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oxygen is given off and sulphuric acid is formed.—Yes, at last only sulphuric acid will remain.

M. Quite right; then the sulphuric acid becomes electrolysed.—What will happen then? You shrug your shoulders? What are its ions?

P. Hydrogen and SO_4''.

M. Right; so, hydrogen is separated out at the cathode. And at the anode?

P. SO_4'' appears there. Ah, it will act just in the same way as in the copper sulphate reaction; oxygen is given off and sulphuric acid is formed.

M. Quite right; i.e., fresh sulphuric acid is always being reformed. So, the visible products of the electrolysis are—?

P. Hydrogen and oxygen.

M. Yes; and they are in the proportion in which they form water; for the 2H of the sulphuric acid appear at the cathode, the one O at the anode. Thus the whole process goes just as if only the water was decomposed and the sulphuric acid took no part at all in the reaction. And, indeed, this was the supposition long ago.

P. How did they find out that it was as you described?

M. They discovered that the sulphuric acid collected at the anode, for it is formed from the SO_4'' which is continually travelling thither. If the sulphuric acid had not taken part in the reaction it would have remained where it was.—In order to become more accurately acquainted with this subject you can repeat our previous experiment (p. 69), using dilute sulphuric acid; only you must take platinum electrodes since iron becomes dissolved.

P. Why is this?

M. If the sulphate ion arrives at a copper, or iron, electrode with which it can combine, then it just enters into combination and the corresponding sulphate, $CuSO_4$ or $FeSO_4$, is formed.

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P. Once again, this is incredibly simple.

M. Just allow the current to pass through sulphuric acid, using copper wires; then you can conveniently observe the effect, because the copper solution, which is produced, can be recognized by its greenish-blue colour (Fig. 13).

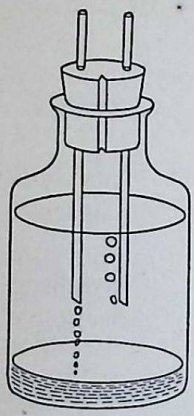

FIG. 13.

P. Then what happens in this case?

M. You must solve that yourself. What are the ions of sulphuric acid?

P. $2H^{\cdot}$ and SO_4''. So the SO_4'' goes to the copper and forms $CuSO_4$, and the $2H^{\cdot}$ go to the other copper and—

M. And evolve as hydrogen gas, for the metals do not, as a rule, unite with hydrogen.

P. Well, the current has already been passing through for quite a time, but I cannot yet distinguish any blue colour.

M. Look through the glass from one side, more especially through the lower portion of the liquid.

P. Yes; it is blue low down. But why there?

M. The solution has formed at the electrode, but has sunk to the bottom because it is heavier than the rest of the liquid, If you look closely and choose a proper light, you can see the solution sinking in streaks.

P. Is there no other test for detecting copper in the solution?

M. There are many. If I, for example, treat copper sulphate solution with sodium hydrate solution a bright blue precipitate is formed. Look here; there it is.

P. What kind of a substance is it?

M. A compound of copper and hydroxyl, which we call copper hydroxide. The reaction is represented by the equation

$$CuSO_4 + 2NaOH = Na_2SO_4 + Cu(OH)_2.$$

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P. The formula appears quite similar to that of calcium hydroxide, $Ca(OH)_2$. Is copper hydroxide also a base?

M. Yes, it is; but a very difficultly soluble one; therefore it appears as a precipitate. Look; if I now add a little of any acid the precipitate dissolves.

P. I made just the same experiment with some liquid from the previous experiment (Fig. 13), but no precipitate was formed.

M. That is because the liquid is a mixture of sulphuric acid and copper sulphate. The sodium hydrate first acts only on the sulphuric acid. Write the equation.

P. $H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$.

M. Right. Only after no more sulphuric acid is left can the sodium hydrate act on the copper sulphate and form copper hydroxide.

P. Why does it not do this first?

M. You should be able to answer that yourself. If copper hydroxide were formed, when the sulphuric acid was still present, what would happen?

P. Ah; I see: the sulphuric acid would dissolve the copper hydroxide, and therefore the latter cannot exist at all, so long as the sulphuric acid is there.

M. Quite right. It is a universal rule that no precipitate can be formed in the presence of another substance which is capable of dissolving it.—But, to continue, this test which you have just learned is of universal application: the hydroxides of most metals are insoluble (i.e., soluble in extremely small quantities), and therefore precipitates are formed if we treat the dissolved salt with the hydrate of sodium or of potassium.

P. Does it matter which we take?

M. Of course not, for if you write the equation with potassium hydrate, instead of sodium hydrate (that is with KOH, instead of NaOH), you obtain just the same result as regards the metallic hydroxide. All that is necessary is to intro-

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duce the hydroxyl ion OH′, into the solution so that the insoluble metallic hydroxide can be formed.—Just make the experiment of precipitating the other metallic salts, which you have prepared, with sodium hydrate, and you will obtain a sight of all their hydroxides.

P. I have made the experiment. All gave white precipitates, with the exception of iron which gave a dirty, green one; while the calcium salt gave none to speak of.

M. Calcium hydroxide, except in large quantities, is soluble in water.

P. Please tell me. I would like very much to repeat the electrolysis experiment. My uncle has given me four dry cells; can I use them for this purpose?

M. Certainly. The two binding-screws on the top are the two poles of the cell (Fig. 14); the current passes, if you connect them with a wire. The constituents of the battery are used up in producing the current; therefore, you must take care never to have the poles connected unless you are using the electricity for some definite purpose.

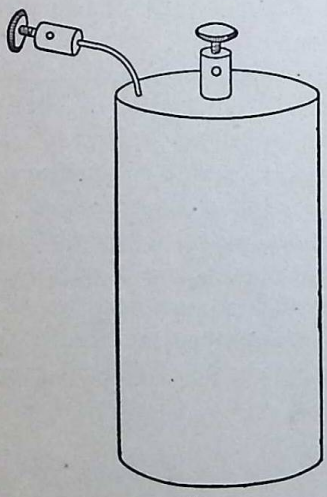

Fig. 14.

P. And when one cell is exhausted I take another.

M. No; you will generally require three cells at the same time.

P. Why?

M. Each cell has a definite electric potential or pressure, (p. 73), and it depends on this how much chemical work it can do. The electrical potential of one cell is not sufficient

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to effect the dissociation of the water in a sodium hydrate or sulphuric acid solution, and therefore we must take several cells.

P. Two horses can pull more strongly than one!

M. Your comparison is a good one, but you must understand the proper way of yoking them together. If you wish to obtain the total electric tension you must always connect the opposite poles with one another. One binding-screw appears in the centre of the cell, the other at the side. Connect, with a wire, the side screw of the first cell with the centre screw of the second, and you have then double the tension between the two remaining screws.

P. But if all three have to be joined up?

M. Then you must connect the side screw of the second cell with the centre screw of the third; you have now treble the tension between the first and last poles of the series.

P. I will now know how to connect the fourth cell.

M. This would be unnecessary, for three cells afford sufficient pressure for all our experiments.

12. THE OXYGEN COMPOUNDS OF CHLORINE.

M. Now, at last, we can leave hydrochloric acid; but we have still something to do with chlorine, for we have yet to become acquainted with its oxygen compounds.—Here I have again set up the chlorine apparatus (p. 6, Fig. 1), and I lead the chlorine into a diluted solution of sodium hydrate.

P. This just produces sodium chloride!

M. Certainly, this is formed; but the reaction is not so simple. Just write down the equation.

P. $NaOH + Cl = NaCl + OH$.

M. Express this in words.

P. Sodium hydrate and chlorine give sodium chloride and hydroxyl.

M. Such an equation does not represent what actually

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occurs; for hydroxyl does not exist as such, but only in combination with other elements. The correct equation is:

$$2NaOH + Cl_2 = NaCl + NaClO + H_2O;$$

read it.

P. Two sodium hydrate and two chlorine give sodium chloride, and a new salt, and water. Why do you write Cl_2 and not $2Cl$?

M. Because chlorine gas has the formula Cl_2 in conformity with its density. The new salt is called sodium hypochlorite. It is the sodium salt of the hypochlorite ion, ClO'.

P. What a long name!

M. Chlorine combines with oxygen in different proportions to form different anions which we distinguish by various names. Here is a table of the names of the anions; the acids, which consist of these anions and hydrogen; and the salts:

Anions.	Acids.
ClO_4'. . . perchlorate ion	$HClO_4$. . . .perchloric acid
ClO_3'. . . chlorate ion	$HClO_3$. . . .chloric acid
ClO_2'. . . chlorite ion	$HClO_2$. . . .chlorous acid
ClO' . . . hypochlorite ion	$HClO$ . . . .hypochlorous acid

Salts.

$MClO_4$. . . . . .metallic perchlorate
$MClO_3$. . . . . .metallic chlorate
$MClO_2$. . . . . .metallic chlorite
$MClO$ . . . . . .metallic hypochlorite

P. That is a long table!

M. You can easily impress it on your memory. All you have to remember, with regard to the acids, is that the termination -ic implies that the compound contains more oxygen than one with the terminal -ous; while, in addition, the prefix per (from a Latin word meaning "more") shows the highest proportion of oxygen, and the prefix hypo (from a

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Greek word signifying "less") means the least proportion of oxygen. Notice, also, that the -ic acids form anions and salts with the suffix -ate; and -ous acids, with the suffix -ite.

P. But we could quite well call the acids "hydrogen chlorate," "hydrogen hypochlorite," etc.

M. Certainly. When you have become an influential chemist you can introduce these names into fashion.

P. Ah! When!

M. In the meantime you must learn the other names because they are still in general use. A similar nomenclature is employed for many other elements whose compounds with oxygen are anions, such are sulphur, phosphorus, bromine, iodine, etc.; if you have taken note of the above rules you will easily understand about many other compounds.—So by passing chlorine through sodium hydrate solution, sodium hypochlorite, as well as sodium chloride, is formed. This liquid is known as bleaching-liquor.

P. Because it bleaches?

M. No; because we can make use of it for bleaching. Just pour some into a test-tube and add an acid, say dilute sulphuric acid, to it. What does it smell like?

P. It smells very disagreeable; I think chlorine had this smell.

M. Quite right. The chlorine has been set free again. Here is the chemical equation; it shows you what happened:

$$NaCl+NaClO+H_2SO_4=Na_2SO_4+Cl_2+H_2O.$$

P. Sodium chloride and sodium hypochlorite and sulphuric acid give sodium sulphate and chlorine gas and water.

M. Quite right; and the chlorine now produced is just that quantity which was used in making the bleaching-liquor. You remember that we were able to bleach with chlorine; we can, thus, also bleach with bleaching-liquor if we add some acid.

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P. Yes; but why do we use this method? We could simply take chlorine!

M. This would do quite well, if we could obtain the chlorine at the place where we were to use it. But a gas is not easy to transport, for it takes up too much space.

P. Still we might use the liquefied chlorine in the bombs, such as you described to me. (P. 8.)

M. This chlorine is too expensive, because it has to be purified and dried. We can use impure chlorine for bleaching-liquor. Besides, if we take calcium hydroxide, instead of sodium hydrate, we obtain a solid compound which is more suitable to use than bleaching-liquor.

P. Is that because it is easier to transport a solid than a liquid substance?

M. Partly that, and partly because calcium hydrate is much cheaper than sodium hydrate. The product is a white powder which goes by the name of bleaching-powder. It smells of chlorine and is employed to destroy, or render harmless, bad smells and putrid matter.

P. I think I have several times seen white powder strewed in places for such a purpose.

M. If there was a smell of chlorine, then it was bleaching-powder.—Now we shall meet an old acquaintance again. If we make bleaching-liquor with a concentrated solution of caustic potash (one part to two of water), and take care to have excess of chlorine: first of all potassium hypochlorite is formed, and then potassium chlorate. Do you remember this substance?

P. Is it the same as we used for the preparation of oxygen?

M. Certainly. I will now show you how it is prepared. To begin with, hypochlorite and chloride of potassium are formed, according to the equation:

$$2KOH + Cl_2 = KClO + KCl + H_2O.$$

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But then the hypochlorite changes into the chlorate and chloride:

$$3KClO = KClO_3 + 2KCl.$$

P. Why does it do this?

M. Because the hypochlorite is not the most stable of the products possible in this reaction. The chlorate is more stable, and therefore it is formed from the hypochlorite.

P. Yes; then why is the chlorate not formed at once?

M. A very natural question. It is because the intermediate stages must be first passed before the last is reached. If you wish to go from one side of the room to the other, you must, in any case, pass over the middle; even if you do not wish to remain there.

P. That sounds quite intelligible, but I still have an uncertain feeling about it.

M. That is not to be wondered at; you will gain an accurate insight into these circumstances only after very much wider and deeper experience.—We can, in this case, pass over the intermediate stage and simply write

$$6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O.$$

P. Why do we use 6KOH here?

M. The second equation contains 3KClO; but here you must use 6KOH. You obtain this number by multiplying the first equation by three, adding the second, and then striking out the equivalent terms which appear on both sides.

P. Then have we the right to strike out these terms?

M. If a formula is on the right-hand side, it means that a substance is produced; if on the left, that it disappears. So if it is produced only to disappear, there is quite a possibility that it is not there.

P. Yes; I understand.

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M. Now the caustic potash solution is saturated with chlorine, for the gas bubbles through without dissolving. And now crystals are already separating out. There will be many more when the solution is cold; because potassium chlorate is much less soluble in cold than in hot water.

P. Yes; I remember copper sulphate acted in the same way (I. p. 21). Then where is the potassium chloride? Some must have been formed.

M. It remains dissolved in the liquid, and can be obtained by filtering off the potassium chlorate crystals and evaporating to dryness the filtrate, which is called the "mother-liquor."

P. Are the two salts completely separated by this process?

M. No; such a "separation by crystallization" is always incomplete, for some of the mother-liquor, containing potassium chloride, clings to the potassium chlorate filtered off. But if we press these crystals, as thoroughly as possible, between filter-paper (so that the mother-liquor is absorbed) and then dissolve them by heating with a little water, fairly pure crystals of potassium chlorate separate out from this solution, (which must be filtered if it is cloudy). I will do this now so that you can repeat it again.

P. Why do you make so many folds in the filter-paper? (Fig. 15.)

M. The solution then runs through quickly. If I use a flat filter-paper it would run through so slowly that the crystals would separate out on the filter. We always use a "folded filter," if the liquid has to pass through quickly. But if we wish to wash a solid substance lying on the filter, we must use a flat filter-paper.

P. Why?

M. Because we cannot wash down the edges of a folded filter.

P. Ah, I understand; the water would flow down the outside and carry over some of the solid with it.

M. Quite right. And in order to purify the potassium

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chloride, I add to what remains after the evaporation of the mother-liquor just so little cold water as will not dissolve the whole of it, filter, and again evaporate the filtrate. What is left is tolerably pure potassium chloride.

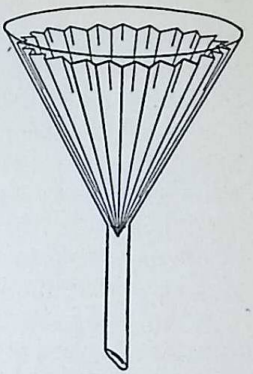

FIG. 15.

P. How is that?

M. Only a little potassium chlorate dissolves in cold water, therefore what there is of it remains on the filter. If we evaporate the filtrate and do not drive off all the water, but leave some of the mother-liquor, the potassium chloride crystals will be quite pure enough. We remove this small quantity of mother-liquor by allowing the mass to dry on filter-paper. The mother-liquor then soaks into the paper and, when dry, we can shake off the potassium chloride crystals.

P. That is a very neat way of doing it. I will make some more potassium chlorate myself, and try to separate the pure salts. Can we use caustic soda instead of caustic potash?

M. That would not suit your purpose. Sodium chlorate is, indeed, formed just in the same way as the potassium chlorate; but it is very easily soluble, and its separation from the sodium chloride mixed with it is more difficult.—But now, take note, I shall show you something of importance. I dissolve some potassium chlorate in water and add silver nitrate solution. You see; the liquid remains clear as water.

P. What is there peculiar about this?

M. Potassium chlorate is a salt and contains chlorine and yet gives no silver chloride precipitate, though all chlorides do. That is because the ions of potassium chlorate are K, and ClO_3'; so with silver nitrate, only silver chlorate, not silver chloride, is formed. You see from this that chlorine

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only gives its characteristic reaction with the silver ion when it is present as the chlorine ion.

P. That is something similar to what you told me about water. It contains hydrogen, but yet is not an acid.

M. Quite right. Water does not contain any quantity of hydrogen ion worthy of consideration. There is, to be sure, a very small amount there, but it is so slight that the ordinary tests for hydrogen are not delicate enough to indicate it.

P. I do not understand.

M. I told you that 0.0015 g. of silver chloride dissolve in 1 litre of water. So this defines the least amount of chlorine ion that we can detect with the silver ion; if still smaller quantities of chlorine are present, no precipitate can be produced. Therefore we say that the "delicacy" of the test is available down to this limit.

P. Have the different tests various limits?

M. Certainly. You can easily detect 1/1000 ccm. of chlorine gas by the nose, while the glowing match test for oxygen can hardly be carried out with less than 1/10 ccm.

P. Yes; now I understand quite well. So it is possible for a substance to be present without our being aware.

M. Certainly; that is the case with every one, up to a certain limit. Therefore we endeavour to discover the most delicate tests possible for each substance.—But let us return to our potassium chlorate. I heat some of the small crystals in a test-tube, allow to cool, dissolve the residue in water, and add some silver nitrate: the characteristic silver chloride precipitate is immediately formed. Explain that to me!

P. I cannot.

M. Write down the equation for the decomposition of potassium chlorate.

P. $KClO_3 = KCl + 3O$.—Ah; now I see: there is potassium chloride, with its ions, chlorine and potassium.

M. Right; you should have said so at once, for you knew about this.

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P. Yes; I was not equal to it.

M. You should have tried to represent what I had done in the form of a chemical equation.

P. Yes; then I would have managed it by myself. I will remember that in future.

13. BROMINE.

M. To-day I will let you off the repetition, but it will all come to the same thing. For the elements which we wish to study, to-day, are so similar to chlorine in their behaviour that, in many cases, in order to answer me correctly you will only require to reply to my questions as if they referred to chlorine. These elements are bromine and iodine.

P. Then do they behave exactly in the same way?

M. No; they differ in some respects. But the compounds of these elements are of such a nature that we obtain their formulæ by putting Br or I instead of Cl.—In the first place, let me show you the element bromine; describe what you see.

P. The flask contains a dark-brown liquid, and the upper part of the flask appears reddish-yellow. Is that because the sides are wet with bromine?

M. No; if you look closely you will find that the bromine, like mercury, is lower round the sides than at the surface. Liquids which wet the glass, such as water or oil, stand higher round the sides.

P. Why is that?

M. Because of the surface-tension. I am sorry that I cannot enter into any details about this remarkable property. So if the yellow colour does not come from the wet glass what else causes it?

P. The vapour, perhaps?

M. You have guessed right. You can convince yourself by opening the flask and fanning the air over the mouth towards you.

P. O, what a horrid smell, even worse than chlorine!

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M. But yet, similar. So bromine is a volatile liquid. It is a rarity, for there is only one other element liquid at the ordinary temperature.

P. Which?

M. Come, you know!

P. I cannot remember one.

M. Mercury.

P. Ah, yes. Forgive my stupidity; of course, I should have known.

M. At any rate, you had the list of the elements in front of you and should have read it through until you came to a metal which you knew was a liquid.

P. Yes; I wish we always knew at once what was the proper thing to do.

M. I am here to teach you that. But let me continue the description. Bromine boils at 60°; but, as water does, gives off vapour even at the ordinary temperature. Since bromine vapour is yellowish-brown we see it; while the colourless water-vapour is invisible—

P. And also has no smell!

M. Right. Let us go into the open air so as not to be annoyed by the pungent vapour. I have here a large, empty (i.e., full of air) jar; I put in a drop of bromine. You see how it changes to a yellow vapour which remains lying on the bottom.

P. So it is heavier than air.

M. Its density is about five times that of air. But if we let the jar stand for some days, the bromine vapour would spread itself uniformly through the atmosphere. In order that it may not escape lay a glass plate, coated with vaseline, on the mouth.

P. How is it that the plate closes it so securely?

M. I have previously ground the mouth of the jar by rubbing it with wet sand on a smooth, cast-iron plate (a flat stone does just as well).

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P. Could I do this?

M. Certainly; all you have to do is to move the jar in a circular path; always keep it vertical and do not let it rock during the rubbing. Hold it low down on the neck, then you will manage all right.—Do you know why the bromine vapour does not remain permanently at the bottom, although it is much heavier than air?

P. Perhaps, because the jar does not stand quite steady.

M. No; it is because all gases mingle of their own free will, if they are in contact with one another. We call this

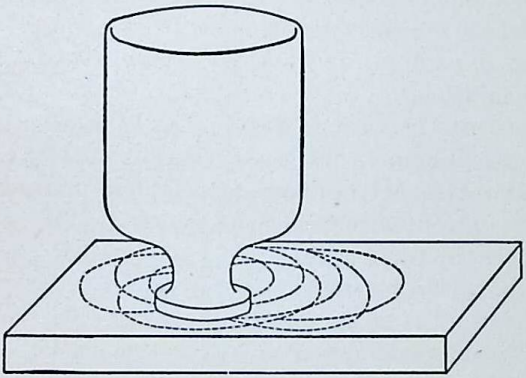

FIG. 16.

phenomenon "diffusion." Now I pour some drops of bromine into about 100 ccm. of water, and shake: a yellowish-brown solution of bromine in water is formed; this we call bromine water.

P. It corresponds to "chlorine water."

M. Right. If I shake up some powdered magnesium with this bromine water, the yellowish-brown colour disappears and, on filtering off the excess of magnesium, I obtain a colourless liquid. What do you think has happened?

P. Probably the bromine and magnesium have combined.

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M. Quite right. The equation is

$$Mg + 2Br = MgBr_2,$$

for magnesium is divalent, like calcium; and bromine is monovalent, like chlorine. The compound is called magnesium bromide.

P. Magnesium bromide is, of course, a salt?

M. Yes; the solution conducts electricity and if the current is passed through, using platinum wires, you can, after a short time, see the yellowish-brown colour of the "free" bromine. What happens in this case? Remember the electrolysis of the hydrochloric acid. (P. 72.)

P. Let me think.—I have it. The bromine ion is changed into bromine because the current leaves the liquid.

M. Right. The bromine ion is an anion, so it travels with the negative electricity. Thus the bromine appears at the place where the negative current leaves the liquid; that is just where the positive current enters the liquid.

P. Yes; the two currents go in opposite directions.

M. What do you see at the other electrode?

P. A white cloudiness.

M. Can you make out what it is? What is the other ion of magnesium bromide?

P. Hm—the magnesium ion. This must yield magnesium.

M. It acts in the same way as the sodium did. (P. 70.)

P. So then magnesium decomposes the water and forms magnesium hydroxide and hydrogen? But yet magnesium powder has no effect on water!

M. Your reasoning is good. Ordinary magnesium is coated with a thin covering of magnesium oxide which is formed from the oxygen of the air; this protects the metal by enveloping it so that no water can get in contact with it.

P. And in the case of the electrolysis?

M. There the magnesium is without any protection, and, therefore, it is attacked by the water; but we only see it in

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the form of its hydroxide which is formed by the action of the water.

P. The very simplicity of the results of electrolysis prevents me from understanding them.

M. They will soon become quite familiar to you, for, as a rule, the reactions are very similar.—Now let us dilute some drops of magnesium bromide solution with water, and add some silver solution.

P. A white precipitate appears, as if there was chlorine ion present.

M. It is silver bromide. The silver ion is also a test for the bromine ion, Br'. But this precipitate is somewhat different, it is rather yellowish; while silver chloride is snow-white.

P. Here we have a true similarity between chlorine and bromine. But in what do they differ?

M. I shall show you later on. In the mean time; look here: I add some chlorine water to the magnesium bromide.

P. It becomes yellowish-brown, like bromine water.

M. Bromine is set free; the equation for this reaction is:

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2.$$

P. So the chlorine has decomposed the magnesium bromide?

M. Yes; the bromine sold on the market is prepared in this way. Magnesium bromide is found, in small quantities, in sea-water and in several of the salts present in nature. It remains in the mother-liquor (p. 107) when the other salts crystallize out.

P. Is it easily soluble?

M. Yes. These mother-liquors are decomposed by just so much chlorine as will allow nearly all the bromine to separate out; any excess must be avoided, because it would contaminate the bromine.

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P. How do we get the bromine out of the liquid?

M. You should answer that question yourself. How do we separate two substances when both are dissolved in the same solution? Think how, in a salt solution, the salt is separated from the water.

P. In that case you evaporate the water. But were I to do this here, the bromine would escape, because it is volatile. You told me that it boiled at 60°, so it would disappear more quickly than the water.

M. Well, that is just the way to effect a separation.

P. Then I would lose the bromine!

M. Why?

P. It would go away, as vapour. You laugh, so I suppose I must think again. Ah, yes; I can cool the vapour and then I can keep the bromine.

M. Right. You must distill the solution of bromine in water. Since bromine is more volatile than water and, besides, has a much greater vapour density, it collects in the first fractions of the distillate and you obtain a large quantity of bromine mixed with a little water.

P. Then what has the greater vapour density to do with it?

M. Just consider. Bromine vapour is nearly nine times heavier than water vapour; if both boiled at the same temperature, then, at the boiling-point, there would still be nine times more bromine in 1 litre of bromine vapour than water in 1 litre of water vapour.

P. Yes; I see that.

M. Therefore you have only to make a calculation. The combining weight of bromine is 79.96; its vapour has the formula Br_2; calculate for me, just now, in what proportion the vapour densities of bromine and water stand to each other at a constant temperature and pressure. First of all, tell me the law regarding vapour densities. (P. 65.)

P. The vapour densities are proportional to the molecular weights. Ah, I see; it is quite a simple matter. Water

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has the molecular weight, 18.02; bromine has 159.92; so the proportion is 159.92/18.02=8.87:1. Once again, the question is much easier than I at first thought.

M. I will now show you a pretty experiment, but as poisonous vapours will be given off, we must make it in the open air. I have here some bromine in a test-tube. I set it upright in a heap of sand, and throw in small chips of very thin tinfoil.

P. O, what a red glow!

M. You see, bromine behaves in a manner similar to chlorine; if it comes in contact with a metal it enters into combination.

P. Just as the magnesium did. Then why was there no red glow in that case?

M. Answer this question yourself, and think of the difference between burning in air and burning in pure oxygen. (I. p. 78.)

P. Ah, I know; in the case of the magnesium, there was little bromine and much water, and therefore the temperature could not rise so high.

M. Quite right. You can now make some salts with bromine water and other metals, and so convince yourself that all give the same reactions as the magnesium bromide; namely, a yellowish-white precipitate with silver solutions and, on the addition of chlorine water, the yellowish-brown colour of the bromine in its free, or elementary, condition. All these solutions contain salts which have one and the same bromine ion.

P. Then we must also be able to prepare bromine salts by the other methods. (P. 88.) Is there a bromine acid to correspond with hydrochloric acid?

M. A good question. Yes; it is called hydrobromic acid. What is its formula?

P. It must be HBr, if bromine and chlorine are similar.

M. Right. Here is a flask containing hydrobromic acid dissolved in water; in the pure state it is a gas, at the ordinary temperature, as hydrochloric acid is.

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P. The solution looks just like hydrochloric acid.

M. And it behaves very similarly. You see; it gives the acid reaction with blue litmus paper. If I add only one drop to a large glass of water, even this very dilute solution acts on litmus. Just make the experiment.

P. I have added one drop to the water; now I put a piece of litmus paper in—but it remains blue!

M. And now I stir, and it becomes red!

P. Ah, how stupid of me to forget this!

M. Because you did you must draw a conclusion for me from this involuntary experiment. Where did the drop of hydrobromic acid, which you put into the water, go to?

P. I think it sank; for if it had remained on the surface it would have spread and come in contact with the litmus paper.

M. Right. Hydrobromic acid solution is considerably heavier than water; the more hydrogen bromide it contains the heavier it is. Now just prepare a solution like that of the hydrochloric acid which contained exactly one combining weight in one litre. (P. 27.)

P. To do this I must first measure out 5 ccm., add a drop of litmus, and let the sodium hydrate flow in from the burette until the red solution turns blue.

M. Yes; you know what to do after that. When you have

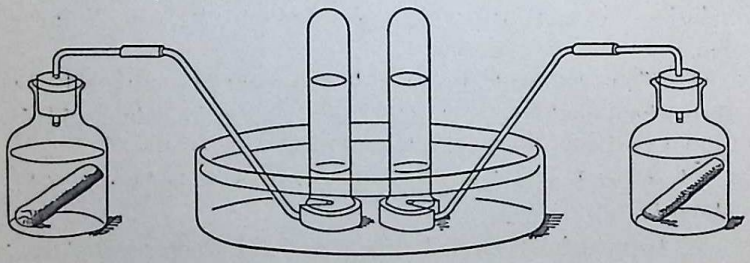

FIG. 17.

prepared the solution, take two small pieces of zinc (of about the same size), place each in a flask, and fit the corks with a

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gas-conducting tube. (Fig. 17.) Then add equal quantities of the two acids, a separate acid in each flask, and observe the speed with which the hydrogen evolves.

P. How am I to do this?

M. Let both the tubes dip into water and count the bubbles, or collect the hydrogen in two cylinders placed over the gas exit. When you have finished, tell me, to-morrow, what you have made of it all. To-day, we will speak a little more of the bromine compounds. How would you prepare hydrogen bromide?

P. Perhaps both burn together, like chlorine and hydrogen?

M. No; we cannot explode bromine and hydrogen, either by the electric spark or by exposure to light. But if we allow a mixture of the two gases to pass over heated platinum, combination takes place, to a certain extent.

P. Then perhaps we could decompose a bromine salt with sulphuric acid?

M. A good idea. But here difficulties come in; sulphuric acid, unlike its behaviour with hydrogen chloride, does not remain unchanged in the presence of hydrogen bromide; but it loses its oxygen, which unites with the hydrogen of the hydrogen bromide and, in this way, bromine is set free. I pour (in the open air!) concentrated sulphuric acid over some potassium bromide; what do you see?

P. A brown vapour, which is bromine. But, apart from this, there is a strong smell.

M. What you smell is the hydrogen bromide. It is colourless, and unites, just as hydrogen chloride does, with the water-vapour of the air, forming a difficultly volatile solution. I hold a wet glass rod in the smell, and then touch a piece of litmus paper with it.

P. There is a red stain, therefore it is an acid.

M. So there is hydrogen bromide there. We will not bother ourselves further with it; it is not of much use. The most interesting thing about it, for us, is its great similarity to

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hydrogen chloride.—You will recognize another similarity between the two elements, if we let bromine act on a caustic soda solution. What does chlorine produce in this case?

P. Sodium chloride.

M. Think!

P. Now, I remember; there are two salts, one with, and one without, oxygen.

M. The best way to remember is to write the chemical equation. Just put bromine instead of chlorine.

P. $2NaOH + Br_2 = NaBr + NaBrO + H_2O$. Is that correct?

M. Yes; read it to me.

P. Sodium hydrate and bromine give sodium bromide and —what do you call it?

M. It corresponds exactly to the chlorine compound.

P. Sodium hypobromite.

M. Right. It contains a new anion, the hypobromite ion BrO'. It has the same bleaching and disinfecting action as the chlorine bleaching-liquor, because free bromine resembles chlorine in this respect. You can easily make some by pouring bromine water into a caustic soda solution, when the brown colour will disappear, showing that the bromine has entered into combination.

P. But the solution does not become quite clear, it remains rather yellow.

M. That is the colour of the hypobromite ions. I will now repeat the experiment with the concentrated caustic potash solution. (P. 104.) I pour in the bromine very cautiously, for a violent reaction takes place. On shaking, the colour disappears each time; and it is only after adding a pretty large quantity of bromine that the brown colour persists in remaining.

P. Quite a quantity of some white substance has separated out.

M. That is a new salt, which corresponds to potassium

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chlorate and is called potassium bromate. What is its formula?

P. If it is similar to the chlorine compound, it will be $KBrO_3$.

M. Yes; that is right. You can, afterwards, purify this salt in the same way as you purified the potassium chlorate, and convince yourself that it behaves in a very similar manner. In particular, its solution gives no precipitate with a silver solution; oxygen is given off on heating; and then the residue, when dissolved in water, gives a precipitate with a silver solution. (Compare p. 108.)

14. IODINE.

M. Well, what have you to show as the result of your experiment yesterday, regarding the speed with which the hydrogen was given off?

P. Practically, nothing. The hydrobromic acid acted just in the same way as the hydrochloric acid. Sometimes the one, sometimes the other, appeared to act the quicker; but there was never much difference between them.

M. Yet there is something very remarkable about this, and you were wrong to call it "nothing." You have seen that other acids behave quite differently; for example, the action of sulphuric acid on zinc is distinctly slower. And what about acetic acid!

P. Yes, there were differences there; but here there are none.

M. Just express the result of your experiment in words.

P. Hydrochloric acid and hydrobromic acid act with equal speed on zinc?

M. That is not quite complete; you must say: equivalent solutions of hydrochloric acid and hydrobromic acid act on zinc with equal speed. Other acids do not; so we really have here a sufficiently remarkable fact; namely, that these acids, which differ from one another chemically, behave in the same way in this special case.

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P. Then what does this fact imply?

M. A good question. To be sure, I can only tell you the answer much later on; but then you will see that it concerns a very important matter.

P. Why did you show me this, if I am to learn nothing more about it?

M. You are to learn more about it, only later on. Then, when we return to this subject, you will have already proved the experimental facts, and therefore you will understand the explanation better. But now let us have a look at iodine. Here is some. It is the third brother of the chlorine, bromine, iodine family, which is known as the halogen or salt-forming group, since they enter into combination with all metals and form salts.

P. But yet this substance resembles neither chlorine nor bromine. Chlorine is a gas, bromine a liquid, iodine is a solid; so the three are as different as they can possibly be.

M. Is chlorine always a gas?

P. No; I think you told me that, under pressure and at a low temperature, we could convert it into a liquid, and even into a solid.

M. Just so. Well, chlorine can be obtained in all these states; so can bromine; and so can iodine; as you will see immediately.

P. But even if they can, they still remain different from each other.

M. To be sure; if they were exactly alike we would only have one substance, and not three. The fact is, the properties of the free elements show a graded difference to each other, though those of their corresponding compounds are similar. These differences can be compared according to the sequence chlorine : bromine : iodine; i.e., according to this standard the properties of bromine lie midway between those of chlorine and iodine.

P. To which properties do you refer?

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M. Almost all. To begin with, take the combining weights: that of bromine is approximately half-way between those of the other two. Chlorine has 35.45; bromine, 79.96; and iodine, 126.85. If you add 35.45 and 126.85, and take the half, you obtain 81.15, nearly equal to 79.96, the combining weight of bromine.

P. Why is the latter not exactly one half?

M. We cannot ask why, or rather, we can expect no answer to such a question. At present, we know nothing at all definite about the laws referring to the numerical value of the combining weights, and can therefore say nothing about an isolated case. Moreover, there are different methods of estimating the mean value between two numbers. The half of their sum is called the arithmetical mean; but we can multiply the two numbers together and calculate the square root from the product: in this way, we obtain the geometrical mean. Just reckon it out.

P. $35.45 \times 126.85 = 4496.8325$; $\sqrt{4496.83} = 67.04$.

M. This value is very different, as you see, from the combining weight of bromine. Before we have some data to go upon we cannot say which calculation is the more applicable. We must, therefore, to begin with, satisfy ourselves with the general facts. You will see these on the subjoined table:

	Chlorine.	Bromine.	Iodine.
Combining weight.....	35·45	79.96	126.85
Boiling-point.....	−33.6°	60°	184°
Melting-point.....	−102°	−7°	114°
Gaseous density.....	0.00317	0.00714	0.0113

P. You were going to show me iodine as a liquid and as a gas.

M. Certainly. I take a dry flask and warm it by keeping it continually moving over a small flame until it has become

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quite hot. Now throw in a small piece of iodine; you see, it immediately melts to a nearly black liquid and—

P. Oh, how splendid! I have never seen such a beautiful violet colour!

M. Iodine vapour is violet. If I shake the flask, you see that the vapour lies heavily at the bottom and keeps rolling to and fro in a sluggish manner. It is nearly nine times as heavy as air. Now let the flask stand for a little: what do you see?

P. The colour gets fainter and fainter, and black particles form on the sides.

M. The iodine vapour is condensing again to solid iodine. Its melting-point is 114°, the boiling-point is 184°. In summer, therefore, it has only a very small vapour pressure, and so when the flask gets cold, nearly all the iodine changes again into the solid state. Just look closely at the black particles.

P. They glitter.

M. Use this microscope.

P. They seem regular, like crystals.

M. That is what they are. I have already told you (I. p. 21) that when substances change into the solid condition, they are, almost always, deposited as crystals. Only they are not always so beautiful as these. If I heat the part where most of them have formed, the violet vapour appears again, but quickly vanishes, and the crystals are deposited on another, colder spot.

P. That is practically a distillation.

M. Quite right; but we call it a *sublimation*, when it refers to the evaporation and recondensation of a solid substance. —Now you know how iodine behaves during changes of temperature; let us see what effect water has on it. What would you expect?

P. Chlorine and bromine dissolve in water, so iodine will also.

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M. We shall try. I take a little iodine, grind it fine in a mortar so that it will dissolve (if it can) more quickly, and pour a pretty large quantity of water over it in a flask. What do you see?

P. It does not appear to dissolve; I see no colour.

M. I pour some of the water into a test-tube; just hold it over a white piece of paper and look in from above.

P. Ah, yes; as I did with the chlorine. I see; some seems to have dissolved, for the water looks brownish.

M. Right; iodine dissolves in water, but only very slightly. I will now make quite certain. I have here a little potato-starch, such as your mother uses in her kitchen. I boil some water in a beaker, and add just a little starch which I have previously stirred up with water.

P. That's the way to make paste!

M. Yes; a very thin paste; for I have only taken a little starch. I pour a single drop of this paste into the iodine solution in the test-tube—

P. That is wonderful! What a beautiful blue!

M. Iodine unites with starch to form a blue substance, so strong in colour that we can detect extraordinarily small quantities. Starch is therefore a very delicate test for iodine—

P. And iodine for starch.

M. Right; you have taken good note that all tests are reciprocal in effect.

P. Is the iodine-starch a salt?

M. No; starch is not a metal. It is a compound consisting of carbon, hydrogen and oxygen; and we really do not know much more about this blue substance than that it is always produced when iodine and starch are brought in contact.

P. Can we use it as a colouring-matter?

M. No; the colour is too transitory for that. Just look here; I warm the test-tube containing the blue iodine-starch—

P. It has become quite colourless!

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M. Now, notice. I place the test-tube upright, with its lower half in cold water—

P. There's the blue colour again. But only in the lower half.

M. I now remove the test-tube, taking care to keep it upright so that the contents do not mix.

P. It remains blue beneath and white above. Yes; but now it is all gradually becoming blue again.

M. What conclusion do you draw from this?

P. That iodine-starch is colourless when warm, and blue when cold.

M. That is not quite correct; for if you look down through the warm solution from above, you recognize the brownish colour of the iodine water.

P. Then the iodine reverts to its usual condition, on warming?

M. I will express what you mean in a better way. When warm, iodine and starch cannot combine, but remain separate from each other in the same solution; but on cooling, they unite and form the blue iodine-starch.

P. Then how is it possible for the same substances to combine at one time and not at another?

M. How is it possible for you to ask me an intelligent question one time and a silly one another?

P. Well that depends on the circumstances!

M. It is just the same here. It depends very largely on the temperature whether certain substances can, or cannot, combine.

P. Ah, yes; now I remember. Iron and carbon burn in oxygen only at a high, but not at a low, temperature.

M. A pretty good comparison. But the conditions there are not the quite same as we have here.

P. Do you mean because here the combination takes place at the low temperature?

M. I mean not only this; but, also, that at the ordinary

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temperature no burning appears to take place, while the fact is that the rate of combination at low temperatures is so slight as to be imperceptible. In this case, on the contrary, there is no combination whatever, no matter how long we may wait.

P. Is it not the case that if iodine and starch unite so quickly at a low temperature, they ought to unite more quickly at a high temperature?

M. Very good; that is an excellent observation of yours. The speed of any chemical process always increases if the temperature is raised. (I. p. 78.) But it does not apply in this case, for here the chemical compound, formed in the cold between iodine and starch, decomposes on heating and forms again on cooling.

P. Can you tell me anything that would help me to understand this question better?

M. That is not very easy, for we are here dealing with the very first case, which has come before you, of the influence of temperature on chemical combinations. Perhaps you will understand me more easily if I remind you that water, which is liquid at a low temperature, becomes a gas at a high temperature, and on cooling again takes the liquid form.

P. But water gives off vapour at all temperatures, only more strongly at high temperatures.

M. Iodine-starch acts correspondingly; a portion dissociates even at summer heat, and, on raising the temperature, this dissociation increases until finally all is decomposed. But we must not occupy ourselves any longer with this subject; only when you know much more about chemistry, we shall return again to these important questions.—Now tell me, why did the iodine-starch, in our experiment, remain blue below and white above?

P. Because it was cold below and warm above.

M. Right. And if I had kept it cold above and warm below?

P. It would have become blue above and white below.

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M. Hm; when I heated the test-tube I brought only the lower part into the flame, and yet not only this portion, but the whole, became white. Moreover, when we heat water in a kettle we always warm only the lower part. How does it happen that the whole of the water becomes hot?

P. Ah; now I know. The warm water is lighter than the cold, and therefore it always rises to the surface. We can, thus, quite well have cold water below and hot above, but not the reverse.

M. Yes; that is right. Now let us return to our iodine-water, and I will show you how we detect starch with it. But in order to dissolve some more iodine in the water and make our experiment go more distinctly and quickly, I add a little (about one fourth) methylated spirits to the water; then much more iodine dissolves and the liquid becomes quite brown.

P. Why is that?

M. Iodine dissolves easily in pure methylated spirits. If we add the good solvent, methylated spirits, to the bad solvent, water, the solvent effect of the mixture varies according to the proportion of the two constituents.

P. Is that always the case?

M. Not always, but very often. Of course, we cannot calculate beforehand the effect of a mixture by measuring out its constituents; but, as a general rule, this method proves effectual.

P. So, here, there is no actual law of nature, because if there were we could always calculate beforehand what was going to happen.

M. Quite right, as regard no previous calculation being certain. All these phenomena, however, obey a law of nature; only it is not a simple one, and therefore we have not yet found it out. I now take my brown iodine solution, and put a drop on a slice of white bread.

P. It becomes quite black!

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M. It is really blue, but the blue is so dark that it appears black. The iodine has combined with the starch, which is in the bread, and has formed the dark-blue iodine-starch. You can, in the same way, prove the presence of starch in potatoes, apples, peas, beans, etc.

P. Is there starch in all these?

M. Yes; and in many other plants besides. If a butcher has cheated by putting flour into his sausages we can detect it by this test; because meat itself contains no starch.

P. Then I can be a wizard, with my iodine solution, and find out secrets!

M. We have found out many more important things with our iodine-starch. More especially, we have discovered that leaves, which have been exposed to the sun, contain starch; while those kept for a long time in the dark contain none.

P. How do you explain this? And why is it so important?

M. I have told you before that the sun works some chemical change in green plants. (I. p. 245.) Now our observations have showed us that the formation of starch seems to be the only result of this work.

P. So, therefore, it is present in leaves which have stood in the sun. But where does it go in the dark?

M. There, it is partly consumed, partly transferred. The leaf, in order to live, must burn up its food with oxygen, as an animal does (I. p. 247); only it makes its own food with the aid of the sun's energy, which an animal cannot do. Now if it has been a long time in the dark it will have used up the provisions stored up in the form of starch, and so we can find none.

P. But how does the starch get into the potatoes? They are under the earth, in darkness.

M. A very good question! The starch gets there in the following manner: The leaf is the factory where the starch is made; if it remained lying there, it would soon block up the space and the factory would be able to produce no more.

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Therefore plants are constructed so that the starch, when made, is carried to another portion where it causes no obstruction and where it is of use. Such portions of plants are, more especially, the seeds and tubers which produce the future plants. At first, these have no green leaves, and so cannot prepare any nourishment; they must, therefore, live on food already present, and this is supplied by the store of starch.

P. And then man comes and carries off this store.

M. That does no harm, for plants produce very much more of such sustenance than they can develop. A cornfield bears from six to eight times as much corn as was planted in it as seed. It is just in this way that plants store up the sun's energy for the use of man and beast.—But now let us return again to the iodine. Can you suggest an experiment to show me that iodine is similar to chlorine and bromine?

P. It can unite with metals?

M. Yes. I shake my iodine solution with powdered magnesium; there, it becomes colourless, just as the bromine solution did. So what has happened?

P. Has magnesium iodide been formed?

M. Yes; i.e., iodine and magnesium have changed into iodine ion and magnesium ion. I filter the solution and add a little bromine-water. What do you see?

P. The brown iodine colour returns again.

M. Now, tell me, how will you convince yourself still more accurately that this really is iodine?

P. By adding starch.

M. Very good. There is still some of the starch paste left. There; it becomes quite dark.

P. But not blue; the liquid appears rather greenish-brown.

M. That is because I added only a little starch, so that just a small portion of the iodine could be changed into iodine-starch. I pour a little of the greenish solution into another glass, dilute with water, and add some more starch—

P. Yes; it now becomes quite blue. It really is iodine.

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M. You can, afterwards, warm this liquid in a test-tube, and convince yourself that the colour disappears on heating and reappears on cooling.

P. Yes; I would like to do this.

M. Now take another portion of the magnesium iodide and add a drop of silver nitrate. What happened in the case of the chlorine ion and the bromine ion?

P. A white precipitate was formed. Here is a precipitate also, but it is bright yellow.

M. You here see how iodine can resemble and, at the same time, differ from the other halogens.—The following will show another similarity: I add a little sodium hydrate to my iodine solution. What do you see, and how do you explain it?

P. The solution becomes clear. So, probably, that salt with the long name has been formed again.

M. Yes; its name is, according to the rule on p. 102, sodium hypoiodite. Write the chemical equation for me!

P. I can do this from memory.

$$2NaOH+I_2=NaIO+NaI+H_2O.$$

M. Right. And if I let the solution stand, the other reaction with the six combining weights of sodium hydrate takes place. Write it down, and read it to me.

P. $6NaOH+3I_2=NaIO_3+5NaI+3H_2O$. It forms sodium—?

M. Sodium iodate. This reaction goes much more easily and quickly with iodine than with the other halogens; so we cannot preserve the hypoiodite; it exists in the solution only for quite a short time.

P. Is there also a hydrogen iodide?

M. Certainly. It, likewise, is gaseous, as hydrogen chloride and hydrogen bromide are; but it condenses to a liquid

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more easily than these, and is also more soluble in water. Moreover, it is colourless like the others.

P. Can I see some?

M. It is not easily made. I have some here, dissolved in water. I have just prepared it. So long as it is quite fresh it is colourless. I pour some into a flat porcelain dish and, you see, it soon becomes brown.

P. This looks like iodine. Add some starch paste!

M. Good; I will. It turns blue; so this actually is free iodine.

P. How is it formed in this case?

M. By the oxygen of the air combining with the hydrogen of the hydrogen iodide. The equation is

$$2HI + O = H_2O + I_2.$$

If I let the liquid stand for some days all the hydrogen iodide changes, in this manner, into iodine and water, and, eventually, the iodine separates out in beautiful crystals. Hydrogen iodide is a weakly-united compound which easily breaks up into its elements.

P. So this reaction is, in some measure, the reverse of the effect of chlorine on water, for, there, the oxygen is displaced. (P. 12.)

M. Quite right; only, in the latter case, we must have the co-operation of sunlight. I will show you, however, that hydrogen iodide is a strong acid, like the other halogen compounds of hydrogen. I pour the solution over a stick of zinc, or magnesium: you see, hydrogen evolves just as fast as if we had taken hydrochloric acid. One drop dissolved in a large quantity of water, gives a solution which immediately colours litmus red.—Well, for the present, we have learned enough about iodine.

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15. SULPHUR.

M. What do you know of sulphur?

P. It is a solid, yellow body.

M. The expression "body" is wrong. What is the difference between "body" and "substance?"

P. Ah, yes; please forgive me. A body is some particular object; while substance refers to all matter having definite properties.

M. Yes; having definite, specific properties, i.e., such as we cannot alter at will. Tell me some of the properties of sulphur.

P. It does not conduct electricity. It burns, and then has a bad smell.

M. That is not quite correct.

P. Well, I am quite certain that burning sulphur has not a nice smell.

M. Sulphur has no smell; whether it burns or not.

P. I do not understand what you mean. Ah, now I know. Then the bad smell comes from the burnt sulphur. That must be some oxide of sulphur.

M. Quite right. It is called sulphur dioxide, because it contains two combining weights of oxygen to one of sulphur. In what form does sulphur dioxide apppear? You don't appear to know. Think; you can smell it.

P. To be sure. Then it must be a gas. Is that right?

M. Yes. We can only smell what reaches the nose, and only gaseous substances get there.

P. So then sulphur cannot vapourize, for it has no smell.

M. That would be a right conclusion were it not for one small difficulty. Do you suppose that you can actually smell everything which the air contains?

P. Certainly; if it has a smell. When, for example, there

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is a bad smell in the room, I open the windows until it goes away, and then whatever caused the bad smell must have gone out.

M. That is just where we disagree. The greater portion has gone out; but when the total amount present in the room has decreased to a certain extent, you can no longer smell it, because your nose is not sufficiently delicate.

P. Please explain that more clearly.

M. The nose can be used to test certain substances, namely, those which produce the sensation of smell. You will ask what this is. We do not yet know much about it; in fact, just as little as we know of the colour sensation produced by certain substances on the eye. Now every test by the nose is limited in extent, and we only perceive a smell if the quantity of the substance rises above a definite amount in a given space. This amount, in the present instance the quantity spread throughout the room, is called the "concentration." Every test fails when the concentration sinks below a certain figure.

P. What do you mean by "fails?"

M. Either the reaction no longer takes place, or we can no longer detect it. In the same way, the burning match, or the glowing charcoal, is a test for oxygen; but yet the match is extinguished in the air, although this always contains an appreciable quantity of oxygen.

P. How do we know that?

M. Because phosphorus can burn in air. Phosphorus is therefore known as a more delicate test for oxygen than the match, or charcoal.

P. So can I smell no sulphur vapour simply because my nose is not sufficiently delicate?

M. Exactly. As a reward for picking up my meaning so quickly, I will prove to you that sulphur can give off vapour, even at the ordinary temperature. Take a polished silver teaspoon, and lay a small piece of sulphur in it. If you

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examine it some days later, you will find that a brown halo has formed round the spot where the sulphur lies.

P. What causes this?

M. The sulphur vapourizes, and the vapour unites with the silver to form a brown-coloured compound, which is silver sulphide.

P. How do you know that it is vapour?

M. If it were merely solid sulphur the stain would be just where the sulphur touched the spoon; but the halo formed by the silver sulphide proves that the sulphur reaches to more distant portions, and it can only do so as vapour.

P. Yes; I understand. Then, is the silver spoon a more delicate test for sulphur than my nose is?

M. Certainly. However, this is partly because you can spend a much longer time over the silver-spoon test than you can when using your nose.

P. Ah, I did not think of that. Does time always have this effect?

M. Not always; but sometimes, if the effect can be steadily concentrated on one spot.—However, we must return to the sulphur. You know it in the solid and gaseous states; let us examine it also as a liquid. Can we melt sulphur?

P. Yes. I have seen, quite distinctly, a piece of sulphur melting when set on fire.

M. You are quite correct. We will just carry out this experiment on a somewhat larger scale. I heat some sticks of sulphur, in a test-tube, over the burner. You see, that sulphur is easily liquefied; it melts at 120°. If I pour out the liquid, it freezes at once to solid, yellow sulphur. Sulphur is, in this respect, quite similar to water. What do you know. about the melting and freezing of water?

P. It melts and freezes at the same temperature, at zero.

M. Right. Only, in the case of sulphur, this temperature is not 0°, but 120°. But now let us apply greater heat to the sulphur. What will happen then?

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P. It will begin to boil.

M. Right; it will, eventually. But we shall see something else before that. Describe what you see.

P. The sulphur gets darker. Do not hold the glass like that, the sulphur will pour out. I say! It is not pouring out. Has it suddenly become solid?

M. Not solid, but very dense. In this respect, sulphur differs from all other substances: on heating the liquid to a certain temperature it becomes denser; while the very reverse is the general rule. We are not exactly certain what causes this.

P. It has become quite dark-brown. Perhaps it is burnt, like paste or milk would be?

M. It looks like that, but it is not the case. If I now remove the test-tube from the flame and let the contents cool, all the previous changes occur in their reverse order. The sulphur is now clear and limpid, and now it solidifies. Burnt milk would not act thus.

P. How would it differ?

M. In this: paste and milk are bodies compounded of various elements and carbon. They decompose at a high temperature and carbon remains behind. (I. p. 224.) But sulphur is an element, and therefore cannot decompose.—Now I again apply heat, so that it passes through all the changes. Eventually, but only when my lamp burns with a big, steady flame, it begins to boil. The vapour is dark reddish-brown.

P. We can scarcely see it.

M. Yes; it condenses again immediately, for sulphur boils at 445°, so the vapour can easily change back into liquid sulphur. I now pour the dark-brown molten sulphur into cold water. Take it out:

P. It is no longer sulphur; it looks like resin, or rubber.

M. Nevertheless, it is sulphur. If we ignite it, it burns just like sulphur; and if we keep it for a long time, it changes

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again into the ordinary, lemon-yellow variety. It is only another form of the element, in fact, it is amorphous sulphur.

P. I do not understand.

M. You have already seen, in the case of carbon, that a substance can assume different forms, without altering chemically. What did I tell you about carbon?

P. Now I remember. Carbon can exist as diamond, graphite, and charcoal; and is, in all cases, carbon.

M. Quite right. And how do you prove this?

P. Let me think; there was something especially satisfactory about it. Yes: if we burn the various kinds of carbon we always obtain equal amounts of carbon dioxide.

M. From equal quantities of the different kinds we obtain equal weights of carbon dioxide. Could this method be also used to test the rubber-like sulphur?

P. If it really is only sulphur, it must yield the same weight as an equal quantity of ordinary sulphur would yield, if both were burnt.

M. Quite right; this is the case. But, on burning, it does not produce the same quantity of heat as ordinary sulphur does, but more. Why is this?

P. Oh, I know, from what you told me about the carbon. The different solid forms are called allotropes, and contain different amounts of energy. Probably the rubber-like sulphur contains more than the yellow, and therefore can give out more.

M. You have remembered that very well.

P. You said that we could look on the energy as a substance which was present, in different amounts, in the allotropic forms. (I. p. 234.) So evidence of these different amounts must appear when the allotropes change into the same compound.

M. Very good; that is just the case. Here is a proof that we were right in comparing the different allotropic conditions with the solid, liquid and gaseous states; for I can convert

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yellow sulphur into its amorphous, rubber-like condition, and this changes again, of itself, into the yellow variety.

P. But this piece is still like rubber.

M. It will become solid and brittle to-morrow or the day after, especially if you let it lie in a warm place.

P. Why does it not change at once?

M. With solid substances, such changes generally take place very slowly. These phenomena are similar to those attending supercooling. (I. p. 233.)

P. Yes, I remember; the same thing applied to the production of diamonds.

M. These two varieties are not the only allotropic forms of sulphur; there are still five or six other solid forms which differ from ordinary sulphur. But I will not show them to you, for they are all unstable at summer temperature and, as a rule, difficult to prepare. Let us rather turn to the substance produced when sulphur burns.

P. The substance with the suffocating smell?

M. Yes. You already know that it is a gas. It is called sulphur dioxide. Therefore it contains two combining weights of oxygen to one of sulphur, and has the formula SO_2. Just write down the equation for the combustion of sulphur. Remember the formula for the free oxygen present in the air.

P. $S+O_2=SO_2$.

M. Right. It follows from this, that the oxygen, and consequently the air also, does not alter in volume when sulphur burns in it.

P. How do you make that out?

M. Look at your own equation. Sulphur is a solid substance. How many molecules of sulphur dioxide are produced from one molecule of oxygen? And what is the law about the molecular volumes of different gases?

P. Ah, now I see. The molecules of all gases are equal in volume; so one molecule of sulphur dioxide occupies the same volume as one molecule of oxygen.

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M. Right. I will make this clear by an experiment. I bend a glass tube in two places, so that the bent pieces run parallel to each other; I pour in some mercury and I now have a manometer. (Fig. 18.)

P. What is that?

M. An apparatus for measuring the pressure. If I suck, or blow into, the lower end, the mercury changes its position, and so I can see what the pressure is in any vessel to which I have attached such a manometer.

Fig. 18.

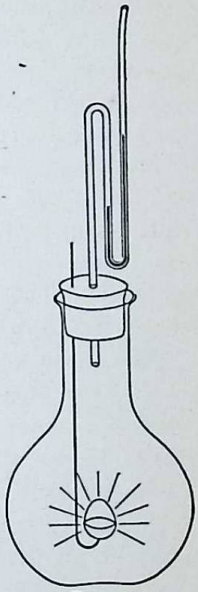

Fig. 19.

P. In fact, this is the same apparatus as that used in demonstrating Boyle's law. (I. p. 190.)

M. Quite right, only this manometer stands erect, without any support. I pass it through a cork which hermetically seals a large flask; the spoon for the burning sulphur (I. p. 77, Fig. 20) is also fixed to this cork. I set fire to the sulphur, and fasten the cork firmly into the flask. (Fig. 19.) Look at the manometer!

P. The mercury rises in the outermost tube. So there is a greater pressure inside the flask than outside.

M. Quite right; that is because when sulphur burns heat is formed; this increases the pressure of the enclosed air. (I. p. 208.)

P. The sulphur has now ceased to burn, and the mercury sinks again.

M. When all is quite cold, the mercury will stand at the

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same level in both tubes, showing that the volume of sulphur dioxide produced occupies the same space as the burnt-up oxygen.

P. How have we the right to say this?

M. If, by chance, double the volume of sulphur dioxide were produced, and we let no gas escape from the flask: what would happen then?

P. The pressure inside would increase. Ah, now I understand, because the pressure does not vary, the new gas must exactly fill the place of the oxygen.

M. Yes. The law that equal molecular weights of gases occupy equal volumes only holds good at a constant temperature and pressure. Equal volumes can hold various molecular weights, but then the pressure and temperature cannot be constant.

P. One more question, please. There was only air in the flask, but this just contains one fifth of oxygen. So is not your conclusion wrong?

M. No; for if, by chance, two fifths of sulphur dioxide had been produced from this one fifth, the pressure would have increased. The volume of pure oxygen would have been replaced by double its volume, representing only an addition of one fifth to the volume of the air; that would have been the total increase. I did not use pure oxygen, because the temperature would have risen so high that the pressure inside the flask would have become too great. I open the flask, and pour in a little water.

P. Some gas with a bad smell is escaping!

M. I shake up the gas with the water, keeping the flask closed. Then when I open it, the outside air presses in with a rush. What conclusion do you draw from this?

P. Oh, I know. The pressure inside has lessened because the gas has been dissolved by the water.

M. Right. Sulphur dioxide is very soluble in water. You can examine this solution by dipping in a blue strip of litmus paper.

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P. Let me do it! It turns red! There is an acid here?

M. Quite right. Sulphur dioxide, itself, is not an acid, for it contains no hydrogen. (P. 16.) So what must have happened when the sulphur dioxide dissolved in the water?

P. It must have got hold of hydrogen from somewhere. Did it take it from the water, and displace the oxygen?

M. It takes it from the water; but it does not displace the oxygen, for no gas was given off. It absorbs the water as a whole, according to the equation:

$$SO_2+H_2O=H_2SO_3.$$

Sulphur dioxide and water give sulphurous acid,—for H_2SO_3 is called sulphurous acid.

P. Can I see some?

M. No; if we try to obtain it from the solution by evaporating the water the sulphur dioxide is also given off, and nothing remains behind.

P. Then how do we know that there really is such an acid here?

M. If we add sodium hydrate, the sodium salt is formed, according to the equation:

$$2NaOH+H_2SO_3=Na_2SO_3+2H_2O;$$

and, on evaporation, this salt, sodium sulphite, can be easily obtained in the form of colourless crystals. In the same way, by taking the corresponding base, or hydroxide, we can prepare any other sulphite salts we please. Their solutions contain the divalent sulphite ion, SO_3''.—Now, take note of a new name. Sulphurous acid is formed from sulphur dioxide and water, so we also call it the hydride of sulphur dioxide.

P. Why do we call it that?

M. Hydride is derived from a Greek word meaning "water," and so denotes a compound of water. Conversely, we call sulphur dioxide the anhydride of sulphurous acid. Anhy-

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dride is the general term for a substance which is formed from some other substance by the removal of water.

P. Are these a special class of bodies, as the acids are?

M. No; I only tell you the names because they are often used. Now I will mention and show you some of the special properties of sulphur dioxide. In the first place, it is very destructive to plant-life.

P. Yes; so I would suppose, because of its bad smell.

M. That is no reason; think of the nitrogen compounds. (I. p. 187.) But, in this case, very small quantities have an effect. For example, nearly all plant-life disappears in the neighborhood of foundries where the preparation of metals from their ores leads to the production of sulphur dioxide. Coal also, which always contains sulphur, gives off an appreciable amount of sulphur dioxide on burning; and since this spreads through the air with the smoke, the trees in a town are very apt to suffer.

P. Yes; I have often noticed that the trees on the promenade lose all their leaves, even in early spring. Is this the cause?

M. Yes; and those, such as firs and pines, which have to keep their leaves for several years, cannot, on this account, be kept in a healthy condition in air of this kind. For the same reason, it is difficult to keep hot-house plants in a room where gas-light is much used, because this, in spite of being purified, contains a little sulphur.

P. What a harmful substance it must be!

M. It also has its good points, for it exercises the same effect on undesirable forms of low plant-life, such as fungus moulds. If we burn a few pounds of sulphur in a mouldy cellar all traces of fungus disappear. Wine casks do not become mouldy inside if we burn some sticks of sulphur in the interior before using them.

P. It is difficult to believe that so destructive a substance can be so useful.

M. Every substance is of use. What we must do is to

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find out its properties; and, perhaps, one of these will serve us for some special effect. That is one reason why we search for, and study so carefully, the properties of substances.—Now, another experiment: fetch me some bright-coloured flowers from the garden!

P. Here they are. I am anxious to see what you will do with them.

M. I place them near a small dish containing burning sulphur and cover everything with a large glass. Notice what happens.

P. I can see nothing. Ah, the rose is fading. And now the other flowers, also. They have all become white! That is wonderful!

M. You here see another property of sulphur dioxide; it bleaches coloured plants.

P. Can we make use of this property, also?

M. You think I will have to answer, no? However, we bleach wool, silk, and straw, in this way, by hanging them in a damp chamber containing burning sulphur.

P. Why do they not use chlorine instead for this purpose?

M. Sulphur dioxide is cheaper; also, chlorine destroys and "tenders" silk and wool. We must leave sulphur dioxide for the present. I shall just add that it changes at $-10°$ into a water-clear liquid. One litre of water, at the ordinary temperature, can dissolve about 50 litres of sulphur dioxide gas.

16. SULPHURIC ACID.

M. The most important compound of sulphur is sulphuric acid. We use it for so many purposes that I had to show it to you and explain about it long ago. What do you know of it? (P. 78.)

P. It is a dense, heavy liquid which develops great heat on mixing with water. It can also extract water vapour from the air.

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M. What are its formula and composition?

P. The formula is H_2SO_4, and it is a dibasic acid, because it contains two combining weights of hydrogen.

M. Good. Do you remember a test for sulphuric acid?

P. Yes. Wood, on being brought in contact with it, becomes black, as if burnt.

M. We can recognize the concentrated acid in that way; but when diluted it does not give this reaction. Why not? What causes the black stain?

P. The wood loses water, as it does on charring. Ah; so if the acid already contains water, it can take no more out of the wood.

M. Right. But do you not remember a test for the dilute acid, or rather, for the sulphate ion, SO_4''?

P. Now I know which you mean. Yes; we obtain a white precipitate with a barium salt, because the barium ion forms a difficultly soluble barium sulphate.

M. Good. That is a test for the sulphate ion. But in a dilute solution of sulphuric acid there are also hydrogen ions present. How do you recognize them?

P. By the usual tests for acids, such as litmus paper.

M. Yes. As the sulphuric acid solution contains both these ions we have to prove their presence by two different tests. What use have we made of sulphuric acid?

P. We prepared hydrochloric acid from kitchen-salt with it.

M. Right. And we use it, in the same way, to prepare many other acids.

P. But how do we make sulphuric acid itself?

M. That is a very important manufacture. It is worked on a large scale. We make it by burning sulphur.

P. But that will only yield sulphur dioxide? (P. 131.)

M. This is first formed. Compare its formula with that of sulphuric acid. What must we add in order to make sulphur dioxide into sulphuric acid?

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P. The formulæ are SO_2 and H_2SO_4. We must add hydrogen and oxygen.

M. We can supply these in the form of water and oxygen from the air. I have, here, the remainder of the sulphur dioxide solution which I made some days ago. If I add some barium chloride solution—

P. A white precipitate forms immediately. Has the sulphurous acid changed into sulphuric acid?

M. Yes.

P. So the way to make sulphuric acid is to let a solution of sulphur dioxide stand exposed to the air?

M. This is a possible, but very impracticable, method. For the reaction takes place very slowly, and a great deal of the dioxide would be lost by evaporation. No; we bring a mixture of sulphur dioxide and oxygen (obtained by burning sulphur with excess of air) in contact with water vapour in large, lead-lined chambers; and add an "accelerator," some substance which causes combination to take place very quickly.

P. Why lead-lined?

M. Because lead is not attacked by sulphuric acid, under these conditions.

P. And the "accelerator"?

M. This is a compound of oxygen and nitrogen; you will learn about it later on. An acid containing 35 per cent of water is formed in these "lead chambers." We have to admit this proportion of water; for, otherwise, the process would not work properly. This acid is called "chamber acid," and is used for purposes for which this percentage of water is no disadvantage. For other effects, the water must be removed.

P. How do we manage that?

M. Just by applying heat; the water distills over and the acid remains behind until it retains only a slight percentage of water. In this way the ordinary concentrated sulphuric acid of commerce is prepared. In recent times

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we have generally used for the preparation of the sulphur dioxide, not sulphur itself, but the iron or zinc compounds of sulphur which are found in nature. These, on burning in the air, likewise form sulphur dioxide and, at the same time, the oxide of the metal.

P. I would like to see this process.

M. Perhaps you will get an opportunity, sometime, of going over a sulphuric-acid manufactory. Meanwhile, I will show you an experiment. I, first of all, burn some sulphur in an iron spoon in a fairly large flask. (I. p. 77, Fig. 20.) Then I blow in steam from a flask of boiling water; I hold a glass rod, on which a drop of concentrated nitric acid hangs, inside the large flask (Fig. 20). You see, a red vapour imme-

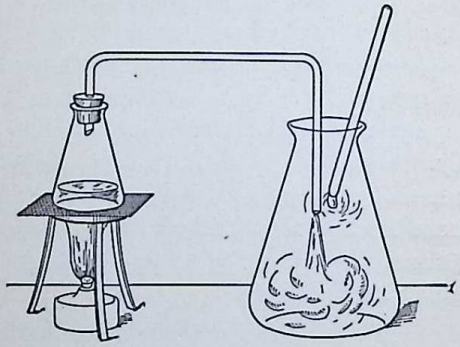

FIG. 20.

diately forms round the glass rod. If, after some minutes, I stop the current of steam and let the flask cool a liquid collects at the bottom, which is strongly acid and gives a large precipitate with barium chloride; therefore, it is sulphuric acid.

P. Yes; so I see.

M. I take a little of this acid, add some powdered sugar, and evaporate the mixture in a porcelain basin over the water-bath. The residue soon turns dark brown, and then black.

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P. Just as the wood did when carbonized by sulphuric acid.

M. Quite right. The sugar is also carbonized; and we can, in this way, detect sulphuric acid. I heat a few other drops strongly. What do you see?

P. A dense, white cloud.

M. The sulphuric acid is changing into vapour and condensing again in the form of this cloud.—Now just look at this remarkable substance in the flask. It looks like cotton wadding and, if I open the flask and expose some to the air on the glass rod, it smells strongly and forms a cloud just as the heated sulphuric acid did.

P. Then what is it?

M. It is sulphur trioxide. I throw some into water—

P. It hisses, as red-hot iron would, and then disappears. Has it dissolved?

M. Yes; and the solution contains sulphuric acid. Just prove this with barium chloride and litmus.

P. So it does. Please explain this to me?

M. It is similar to the case of sulphur dioxide and sulphurous acid. Repeat what I told you about them. (P. 139.)

P. Sulphur dioxide is a gas which, on dissolving in water, unites with it to form sulphurous acid.

M. Sulphur trioxide is a solid, an easily volatile solid, which, on dissolving in water, unites with it to form sulphuric acid. Its formula is SO_3, as the name implies. So its action on water is represented by the equation—

P. Please let me write it:

$$SO_3 + H_2O = H_2SO_4.$$

But how about the hissing?

M. That is caused by the great heat developed in this reaction. Sulphur trioxide is, for this reason, a dangerous substance; it must be stored and handled with great caution.

P. Why does it give off fumes?

M. Because it absorbs water vapour from the air and

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forms the difficultly volatile sulphuric acid; this cannot exist as a vapour, at the ordinary temperature, and must therefore condense in the form of a cloud.

P. How do we obtain the trioxide?

M. From the dioxide and oxygen.

P. Then it must be formed when sulphur is burnt!

M. Quite right; it is; but just in very small traces. Sulphur dioxide and oxygen combine only extremely slowly, and if we wish to obtain a yield in any quantity we must use an accelerator.

P. What! Another accelerator! Which?

M. We can use finely divided platinum, or even iron oxide. I have here, in this wide tube, some asbestos coated

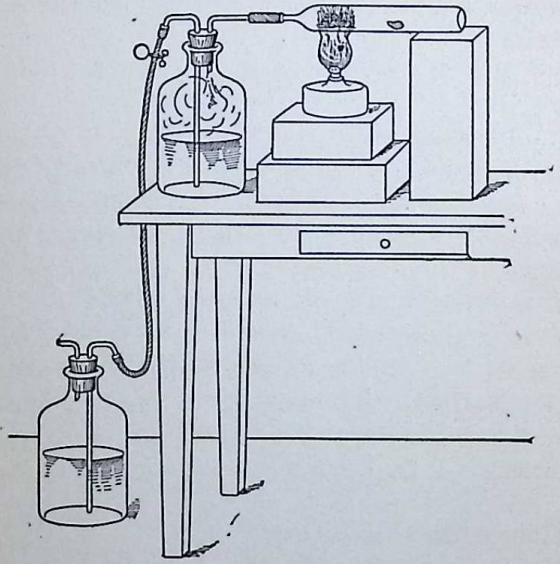

FIG. 21.

with finely powdered platinum. I apply heat with my burner and, at the same time, draw a slow current of air through by means of the two jars already used in I. p. 149, Fig.

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28. Now I insert a small piece of ignited sulphur. It burns, forming the dioxide; but this, on coming in contact with the platinum, changes into the trioxide, which appears in the jar as a dense, white cloud.

P. Can we not collect the trioxide?

M. Would you like to make some yourself? You had better postpone doing so until you have become more expert.

P. What a pity!

M. Sulphur trioxide is, at the present time, prepared in very large quantities by a process similar to the above, as it is used for many purposes in technical chemistry. It is called the anhydride of sulphuric acid. Why?

P. I know, from what you said about sulphur dioxide. It is because we obtain it by the removal of water from sulphuric acid:

$$H_2SO_4 - H_2O = SO_3.$$

M. Good. Now I will tell you something more about the sulphates, or salts of sulphuric acid. It is a dibasic acid and can therefore form two kinds of salts, according to whether one, or both, of the combining weights of hydrogen is replaced by a metal. In the first case we have an acid salt; in the second, a neutral salt.

P. What do these names mean?

M. Let us just write down the formula of the acid salt; it must be $NaHSO_4$, since only one hydrogen is replaced by sodium. I have some of this salt here. It is a white, crystalline substance. I dissolve some in water and test with litmus paper—

P. It immediately turns red.

M. Yes, because, since only one hydrogen is replaced by sodium, the other is not prevented from giving the hydrogen ion reaction.

P. Is hydrogen given off with magnesium?

M. Certainly. Just make the experiment.

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P. Yes; it evolves pretty fast.

M. So you see, the hydrogen still present is really the acid hydrogen. The taste, also, is sour. This is just why these kinds of salts are called acid salts. On the other hand, there is no hydrogen present in the other, the neutral, sodium salt, Na_2SO_4; therefore it does not give these reactions. Here is some of this salt. Perhaps you know it already. It is called *Glauber salt.*

P. I once had to take some Glauber salt when I felt ill. It did not taste nice. How did it get this funny name?

M. Because a German physician, named Glauber, esteemed its medical properties very highly and introduced its use. Here you have a solution of the salt;—no, you need not drink it; but you must examine if it is neutral to litmus and shows no acidic properties. Also, you can prove for yourself that it gives a precipitate with barium chloride. This indicates that the sulphate ion, SO_4'', is present. (P. 91.)

P. Yes; everything is as you said.

M. We will now say good-bye, in the mean time, to sulphuric acid. It is not found, as an acid, in nature (except in small quantities near volcanoes); but its salts, the sulphates, are widely met with, always in the form of neutral sulphates. Besides Glauber salt, *Epsom salt* and *gypsum* are sulphates.

P. Please tell me more about them.

M. I will, later on, when dealing with the metals.

17. HYDROGEN SULPHIDE.

M. To-day, we must have our lesson in the open air.

P. Is that from fear of an explosion or because of the smell?

M. Because of the smell. Just smell this bottle.

P. Phew; like a rotten egg. Is this another sulphur compound?

M. Yes; it is hydrogen sulphide, H_2S. It is a gas, fairly

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easily soluble in water. This colourless liquid in the bottle is a solution in water. I pour some into a beaker and set it aside; you will soon see why. Meanwhile, tell me, is hydrogen sulphide combustible?

P. How am I to know that?

M. Very probably the formula will give some indication. What does this substance consist of?

P. Sulphur and hydrogen. Yes; both these are combustible; so the compound is, also.

M. Quite right. We will make some and set it on fire. In order to prepare hydrogen sulphide we use this black substance, iron sulphide, and an acid, say hydrochloric acid. They react according to the equation

$$FeS + 2HCl = H_2S + FeCl_2.$$

P. That appears to be just the same as the decomposition of a salt by an acid.

M. Very good; that's what it is. Hydrogen sulphide in an acid, just like hydrogen chloride; and iron sulphide is its iron salt.

P. Then could we also use sulphuric acid instead of hydrochloric acid?

M. Certainly. Just write the equation.

P. $FeS + H_2SO_4 = H_2S + FeSO_4$.

M. Good. For that you can help me to set up the apparatus. What sort of one shall we use?

P. Perhaps one like that employed in the preparation of hydrogen (I. p. 135, Fig. 24)? Is the hydrogen sulphide given off in the cold?

M. Yes; for it is a gas, and the iron sulphide is easily decomposed. So we set up the same apparatus as we used for the hydrogen; only, instead of the ordinary funnel, we take one fitted with a cock. Fig. 22.

P. What is the use of that?

M. So that we can let the acid flow onto the iron sulphide

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drop by drop in order that we may not obtain too much hydrogen sulphide. When we have enough we can close the cock. Then we will not make more than is necessary of this evil-smelling gas.

P. Well, everything is now connected.

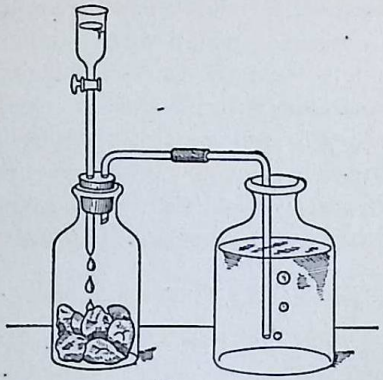

FIG. 22.

M. I let the hydrochloric acid drop slowly onto the iron sulphide. I lead the gas into a jar of water.

P. But it does not appear to dissolve. Ah, of course; first of all, air only comes out of the flask. Now I can smell something!

M. I will make an experiment at once with the small quantity of hydrogen sulphide which is escaping. I hold a newly polished copper coin in it.

P. It becomes quite dark, nearly blue-black.

M. That is copper sulphide. Copper extracts the sulphur from hydrogen sulphide and sets the hydrogen free, just in the same way as zinc acts on hydrochloric acid. Now I take a silver, instead of the copper, coin—

P. It also becomes black! Does a similar reaction take place?

M. Yes; silver sulphide is formed.

P. There is the smell of bad eggs again. I say, if we eat

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an egg with a silver spoon just the very same dark stain appears as the silver coin showed just now. Is it from the same cause?

M. Certainly. The constituents of the egg, especially the white part, contain sulphur in chemical combination; and this is readily given off as hydrogen sulphide, to some extent when the egg is boiled, but still more when it gets rotten. Hydrogen sulphide is what you smell in a rotten egg.

P. Then, actually, hydrogen sulphide does not smell of rotten eggs, but rotten eggs smell of hydrogen sulphide.

M. That is quite a correct conclusion.—Now we have made sufficient hydrogen sulphide. We fix a pointed platinum burner onto the gas tube (I. p. 145, Fig. 27) and set fire to the gas.

P. Why did you not do so at once?

M. Hydrogen sulphide forms an explosive mixture with air, like hydrogen does, and we would have had a very unpleasant explosion. What do you see?

P. The flame is blue; more like the sulphur than the hydrogen flame.

M. That is, so far, correct. Now I hold a large, dry beaker over the flame—

P. It gets dim with moisture, so there is hydrogen in the gas.

M. Quite right. But now I hold a sheet of glass in the flame, moving it to and fro so that no one spot becomes too hot.

P. A white efflorescence forms on the glass. What is it?

M. It is sulphur. If I lower the flame, only the hydrogen burns and the sulphur cools so quickly that it cannot ignite. The same thing happens in the ordinary candle-flame, only there it is the carbon which separates out.

P. But this fog is white; not yellow, like sulphur.

M. That is because it is so finely divided. You know that a substance looks lighter the more finely it is ground. (I. p. 9.) You will see the sulphur still more distinctly if I pass the

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hydrogen sulphide through a heated tube. Then a large proportion of the compound decomposes; sulphur separates out and hydrogen passes on. You can see the yellow particles of sulphur.

P. Can we, conversely, make hydrogen and sulphur combine to form hydrogen sulphide?

M. A little is formed if we lead hydrogen through strongly heated sulphur. Now just look at the hydrogen sulphide solution which I previously placed on one side, in a beaker.

P. It has become quite cloudy, because a white substance has separated out.

M. This is also sulphur. The oxygen of the air has formed water with the hydrogen, and the sulphur has been set free:

$$H_2S+O=H_2O+S.$$

P. And it is white, on account of its finely divided state.

M. Right. Since hydrogen sulphide loses its hydrogen so easily it acts as a strong *reducing agent*, i.e., it extracts oxygen from other substances, or gives up hydrogen to them. We can use this property to prepare hydrogen iodide from iodine. I have some iodine here, immersed in water. I pass in hydrogen sulphide.

P. A white cloudiness is immediately formed. That must be the sulphur again?

M. Correct. Write the equation.

P. Hm; hydrogen sulphide contains two hydrogen atoms, and iodine requires only one. Ah, I have it:

$$H_2S+2I=2HI+S.$$

M. Quite right. Just watch our experiment.

P. Every time you shake, the liquid becomes brown and then turns white again.

M. Each time I shake, fresh iodine dissolves and then changes into colourless hydrogen iodide, the white sulphur

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being thrown out. I dip in a piece of litmus paper, it immediately turns red. The hydrogen iodide did that.

P. Is not hydrogen sulphide also an acid?

M. Yes; but a weak one. If I dip litmus paper into hydrogen sulphide solution, it does not become bright red, but only "wine-red," as happened with carbonic acid (p. 23). Now I will show you the most important reactions of hydrogen sulphide. I have here solutions of the various metallic salts, and I add some hydrogen sulphide solution to each. Tell me what metallic salt I take, and what sort of a precipitate is formed.

P. Zinc, white. Cadmium, yellow. Antimony, yellowish-red. Bismuth, brown. Lead, dark brown. Copper, dark brown. Silver, brown. What are these precipitates? Do all metals give similar ones?

M. The precipitate is, in each case, the sulphur compound of the metal. Those you have seen are the strongest, or darkest, in colour, and so are easily recognized. Therefore, we use hydrogen sulphide to detect the various metals, or rather their ions, for it is as such that they are present in their solutions. Just write down how, for example, copper sulphate is decomposed by hydrogen sulphide.

P. I will try.

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

That must be right? Sulphuric acid is formed.

M. You are quite correct. I told you that hydrogen sulphide is a dibasic acid. The compound CuS, copper sulphide, is its copper salt. When an acid acts on a salt of another acid and forms a salt with the metal then this other acid must be set free. (P. 81.)

P. But you told me that hydrogen sulphide was a weak, and sulphuric acid a strong, acid. How then can the hydrogen sulphide drive out the latter?

M. Because copper sulphide is an extremely insoluble salt.

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Even the very small quantity of copper sulphide, which the weak hydrogen sulphide manages to form, cannot remain in solution. Therefore, much the greater portion is thrown out in a solid state and fresh copper sulphide must be produced. This also precipitates, and eventually all the copper changes into copper sulphide if there is sufficient hydrogen sulphide present.

P. But, if I have understood you correctly, some copper sulphide must always remain in solution?

M. Quite right. That is just what happens. But this quantity is so small that we cannot weigh it, and therefore it is, for most purposes, a negligible amount. Only in certain very delicate experiments this quantity has to be taken into consideration and estimated.

P. That does not exactly explain to me how, so to speak, something can be present, and yet not present.

M. Have you not often looked through a microscope and convinced yourself that we can see with it numerous things which are invisible to the naked eye?

P. Yes. I understand the comparison.

M. I will show you some more experiments which will make the matter clearer to you. I have here the white precipitate from the zinc solution. It was a zinc sulphate solution, and the reaction is similar to the above copper equation, namely:

$$ZnSO_4 + H_2S = ZnS + H_2SO_4.$$

Only zinc sulphide is much more soluble, and therefore all the zinc is not precipitated, even when I add excess of hydrogen sulphide. The liquid smells of hydrogen sulphide, consequently it is present in excess. If I filter, and add a little potassium hydroxide solution to the clear filtrate, a further white precipitate of zinc sulphide is formed.

P. Please, where does that come from?

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M. I will show you immediately. I take some of the white precipitate from the filter, mix it with water, and add some dilute sulphuric acid.

P. It becomes quite clear! What has happened?

M. Read the equation, which I have just written down, backwards.

P. Sulphuric acid and zinc sulphide give hydrogen sulphide and zinc sulphate. Is that it?

M. Yes. Both these reactions are possible; and it depends on circumstances which side has the ascendancy. If there is much hydrogen sulphide and zinc salt in the solution then zinc sulphide and the acid are formed; if there is much acid present then the zinc salt and hydrogen sulphide are formed. The conditions here are the very same as those attending the iron, iron oxide, hydrogen, and water reactions. (I. p. 143.)

P. Please explain it more clearly to me.

M. I have still some of my zinc salt solution. I add first sulphuric acid, and then hydrogen sulphide. You see, there is no precipitate. There is so much acid already present that the reaction cannot now go from left to right. But if I neutralize the acid with caustic potash solution, the precipitate immediately appears.

P. Ah, has that the same effect as the reaction which I could not understand before?

M. Yes. So much acid was produced by the precipitation of the zinc sulphide that no more zinc sulphide could be thrown down. Then, when I neutralized the effect of the acid present with caustic potash, more zinc sulphide could precipitate.

P. This will require some thought before I can understand it.

M. We will meet with many another similar case as we go along. Just note this general rule: the consummation of every reaction is limited according to what is produced.

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Very often this limitation is imperceptibly slight, but in many cases it is very noticeable.

P. Please tell me, is iron sulphide also a salt of hydrogen sulphide?

M. Certainly. Why do you ask?

P. Then the preparation of hydrogen sulphide in our apparatus is exactly similar to the reversed reaction in the above zinc sulphide case; for we could have prepared it according to this equation:

$$FeS + H_2SO_4 = H_2S + FeSO_4.$$

M. Very good. I find that you are beginning really to study chemistry. Iron sulphide is still more soluble than zinc sulphide, and therefore we do not obtain any precipitate on bringing together hydrogen sulphide and a salt of iron. I have here a solution of iron sulphate, the ordinary pale-green *copperas*. I add some hydrogen sulphide solution—

P. Nothing happens. But if you were to add caustic potash—

M. Right. A dark-green precipitate of iron sulphide is immediately formed. This shows you exactly the opposite side of the question: iron sulphide cannot exist at all in the presence of acids, and therefore it gives off hydrogen sulphide with acids. Conversely, if you tried to prepare iron sulphide from the iron salt and hydrogen sulphide an acid would be formed, but this would dissolve the iron sulphide, therefore no iron sulphide is precipitated.

P. But it precipitates if we take away the acid with caustic potash?

M. Right. It would be well for you to study these processes closely, for they afford a ready means of enabling you to know how to separate different metals from each other in analytical chemistry. Some are precipitated by hydrogen sulphide; others, like iron, are not. Such of the latter whose salts are soluble in water can be thrown down by potassium

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sulphide, K_2S, or by sodium sulphide, Na_2S. Write the equation with iron sulphate.

P. $FeSO_4 + K_2S = FeS + K_2SO_4$.

Ah, I see, no acid is produced in this case.

M. Quite right. Let me say, in conclusion, that the sulphides of the heavy metals are very plentiful in nature. The most important are the ores of lead, copper, and silver.

P. What is an "ore?"

M. Ore is the name given to the compounds of metals which are found in nature. Iron-ores, for example, are mostly sulphur compounds of iron. The individual metals are prepared from these natural compounds by chemical means; metallurgy is one of the oldest branches of experimental chemistry. In order to convert the sulphur-ores into the metals we roast them.

P. What! To make them eatable?

M. Roasting here means heating in the air. The sulphur then burns to sulphur dioxide—

P. And is used in the preparation of sulphuric acid?

M. Quite right. The metal is generally converted into its oxide.

P. That does not help us much.

M. It does; for we can obtain the metal by heating the oxide with carbon; this unites with the oxygen and forms oxide of carbon.

P. Why do we employ this roundabout way? Can we not remove the sulphur directly?

M. No; we do not yet know a sufficiently cheap method of doing this. But let us leave this subject. We shall return to it, later on, when dealing with the metals.

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18. NITROGEN AND NITRIC ACID.

M. Do you remember anything about nitrogen?

P. Yes. It is a colourless gas, without smell, and is the chief constituent of the atmosphere, of which it forms, I think, three fourths.

M. Four fifths, or more accurately .79: otherwise you are correct. What else?

P. Nitrogen is mixed, not combined, with the oxygen of the air. It, as a rule, forms few compounds.

M. It forms very many, but does not unite readily, i.e., it is difficult to make it combine. Do you know *saltpetre?* It is a compound of nitrogen.

P. Is that the white salt which we use for fireworks? Do they not also make gunpowder of it?

M. Yes. Saltpetre is the potassium salt of nitric acid, with whose formula (p. 42) and composition you are already familiar. The formula of nitric acid is HNO_3: so what is the formula of its potassium salt?

P. Let me think. O, it is quite simple; KNO_3.

M. Right. Saltpetre contains potassium, nitrogen, and oxygen. I will show you the nitrogen first of all. I mix some saltpetre with ten times its weight of powdered iron, fill a test-tube one third full of the mixture, and heat gently, after loosely inserting a cork. How will you recognize the nitrogen?

P. So far as I remember, it has no special characteristic. Yes, it has; it extinguishes a flame.

M. Right. I dip a lighted match into the upper portion of the test-tube—

P. It continues to burn—now it goes out. You again light the match; now it goes out immediately. I suppose, when you first tried, sufficient nitrogen had not been produced? Please explain exactly what happened.

M. The iron has taken the oxygen from the saltpetre, and

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the nitrogen had to escape because it does not combine either with potassium or iron.

P. Then what has become of the potassium?

M. It, like the iron, remains behind with a small portion of the oxygen as potassium oxide.

P. The iron is now iron oxide?

M. Quite right. It is partly converted into iron oxide. Of course, only partly; for I have taken much more iron than was necessary for the oxygen present, because then the reaction goes more smoothly. We will throw the residue, when cold, into water; then, if I test the solution with red filter-paper—

P. It becomes blue. So a base is there. Perhaps potassium hydrate?

M. Yes. Potassium oxide has the formula K_2O, and gives with water—

P. Let me find out!

$$K_2O + H_2O = 2KOH.$$

Yes; that's it!

M. Now we have still to see the oxygen. I heat a little saltpetre, as strongly as possible, in a test-tube, and oxygen is eventually given off. I insert a glowing match—

P. It burns up. Yes; I have now seen all the three elements. But how am I to know whether there are not others besides these in saltpetre?

M. We can only find that out by accurately estimating how much potassium, nitrogen, and oxygen we can obtain from a given quantity. If the sum of the three weights equals the weight of the saltpetre taken no other element can be there.

P. Can you show me how this is done?

M. I can; but it would be a long and difficult process and you would not understand the various stages. So you must take this, like so many other things, on trust. Later on you can, if you like, prove it for yourself. We will now make nitric acid from saltpetre. What else must we take for this purpose?

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P. I do not know.

M. Just think; how did we make hydrochloric acid from kitchen-salt (p. 83)?

P. By heating with sulphuric acid. Then is nitric acid volatile also?

M. Yes. It boils at 86° when it is pure. If it contains water the boiling-point is higher, but never above 120°. Just write down the equation for me. It is similar to the hydrogen chloride one.

P. $2KNO_3+H_2SO_4=K_2SO_4+2HNO_3$.

M. Right. We will put it to a practical use. Calculate from the combining weights how much of each substance we require to take.

P. $2KNO_3$ is $2\times(39.15+14.04+48)=202.38$; $H_2SO_4=2.02+32.06+64=98.08$.

M. Good. That shows about half as much sulphuric acid as saltpetre. But I shall take nearly equal quantities; the process then goes much better.

P. Why?

M. You remember that sulphuric acid is dibasic. Well, under the conditions which prevail in this reaction, the acid salt (p. 147) forms much more easily than the neutral salt; and in order to obtain the latter I must double the quantity of sulphuric acid. I shake the powdered saltpetre into a retort, and pour in the sulphuric acid on the top. I let the retort stand for some time, with the neck upright, so that the sulphuric acid may penetrate through and through.

P. Why do you not rather take a flask, like the one you used for the hydrochloric acid? (P. 83.)

M. Nitric acid vapour should only be allowed to come in contact with glass because it oxidizes and destroys all organic substances, such as cork or rubber. I let the neck pass into a flask, kept cool by water (Fig. 23), and begin to distill cautiously.

P. Is the vapour of nitric acid yellow?

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M. Because the inside of the flask is yellow? No; nitric acid vapour is colourless. But nitric acid loses part of its oxygen extremely readily, and then brown gases are formed. A trace of dust is quite sufficient to produce these vapours.

P. Now yellow drops are coming over.

M. The same thing applies to these. Pure nitric acid is colourless, like water; but it dissolves the yellowish-brown vapour and then becomes yellow. I continue to distill cautiously until I have a little acid, and then I let everything cool. The acid is very corrosive, so be careful.

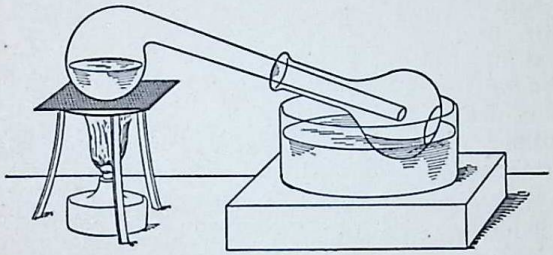

FIG. 23.

P. What are those fumes in the neck of the retort?

M. They are from the nitric acid which, after I had removed the receiving flask, reached the air and became damp. I told you that, when dilute, the acid boils at a higher temperature than when pure; the nitric acid vapour absorbs water from the air, is changed into a difficultly volatile acid, and condenses in clouds. (P. 145.)

P. Then the acid would not fume in dry air?

M. Quite right. It would not. If I put a little concentrated sulphuric acid into a large flask and spread it over the sides, by shaking, the air inside soon becomes dry. Now I hold a drop of nitric acid (which fumes strongly in ordinary air) on a glass rod inside—

P. Yes; the fuming ceases.

M. Now you shall prove to me that the liquid is an acid.

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P. I merely require litmus paper to do this.

M. I will use some. What do you see?

P. It turns yellow, not red. What is the matter?

M. I told you that nitric acid oxidizes everything it can. It has oxidized the litmus.

P. Well, what are we to do now?

M. We put a drop of the acid into a glass of water, and stir. Now try.

P. The paper turns red. Why is it not oxidized this time?

M. Nitric acid only oxidizes quickly when it is concentrated. Diluted with water it acts so very slowly that we can hardly notice any effect.

P. And litmus gives a reaction with very dilute acids.

M. We make great use of this oxidizing effect of nitric acid. I place a drop on a piece of copper—

P. Bubbles rise, and a yellow vapour is formed. But the drop turns green, then blue. Ugh, the vapour smells bad!

M. Take care not to inhale it; it is very poisonous. What do you suppose the greenish-blue substance in the drop is? What is formed from a metal and an acid?

P. A salt, is it not? Yes; and hydrogen is given off. What is the yellow vapour?

M. In this case, hydrogen is not given off, because it is oxidized to water by the oxygen of the nitric acid. The yellow vapour is produced from the nitric acid by the removal of oxygen. What is the name, and formula, of the salt which is formed?

P. It is called copper nitrate. And the formula—I must first look up the symbols for copper—is $CuNO_3$.

M. Wrong. Copper is divalent, so the formula is $Cu(NO_3)_2$. You see, this salt has the same bluish-green colour as the other copper salt which you prepared. (P. 89.) This is the colour of the copper ion.—If I now wash the spot where the drop lay you can see that the acid has eaten deeply into the copper. We use this property in stereotype printing; a

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copper plate is first coated with varnish, the design is sketched on this with a needle, and then the metal is etched with nitric acid. Prints prepared by this method are, therefore, called etchings.

P. There is one point I do not understand. When we etch in the lines they are deepened, and, on printing, they remain white, so we obtain a "negative" picture with white strokes and a black back-ground.

M. We print such plates differently from letters. We use a pretty strong colour, rub it into the impressions on the plate, and then clean the surface. The colour remains only in the depressions, and when a white sheet of paper is applied with strong pressure the colour is imprinted on the paper. Therefore such plates cannot be employed in printing-presses for type.

P. But are not the poisonous yellow vapours given off during the etching with nitric acid? Why do they not use hydrochloric, or sulphuric, acid in preference? These would simply produce hydrogen.

M. They do not dissolve copper.

P. Why is that?

M. Copper cannot displace hydrogen from these acids because it itself is displaced by hydrogen from its salts. But if the hydrogen is always immediately removed by the oxygen of the nitric acid, as soon as the slightest trace is formed, then the copper can go into solution. Silver acts in the same way. Here is a small piece; I pour some dilute nitric acid over it in a test-tube. On warming, the characteristic yellow vapour appears and the metal dissolves. What has been formed?

P. A silver salt. You took nitric acid, so it must be silver nitrate. Wait, it ought to give a precipitate with hydrochloric acid!

M. Quite right. Just see that it does.

P. Do all metals dissolve in nitric acid?

M. Nearly all. Of those you know, only gold and platinum do not. We can dissolve out the silver with nitric acid from

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a mixture of gold and silver, and the gold remains behind.—Now I will show you another instance of how easily nitric acid gives up its oxygen. I take a glowing lump of charcoal and dip it into the concentrated acid.

P. That is very remarkable! The carbon is burning, though wet!

M. The most important uses of nitric acid are due to this readiness in yielding up its oxygen. It serves as an oxidizing agent in many processes.

P. In fact, the solution of metals depends on its power to oxidize the hydrogen.

M. Very good. I must now tell you something about the salts of nitric acid, the nitrates. Potassium nitrate, or saltpetre, has been known for a very long time.

P. Do we not find it in the earth?

M. Not exactly; it is not a mineral which has lain there for thousands of years, but a substance which is continually being produced. Nitrates are formed at places where organic substances containing nitrogen, more especially the excreta of animals, are decomposed by the action of the air. If a potassium salt, say from the ashes of burnt wood, is added we can extract the saltpetre with water from the mixture and obtain the crystals by evaporation. This was how we used to get the saltpetre required for the preparation of gunpowder and nitric acid.

P. And now?

M. In the second half of last century they discovered large quantities of another nitrate, sodium nitrate, in Chile, South America. Since then this has become the most important supply and the source of all other nitrates, such as nitric acid. However, the largest proportion of this *Chile saltpetre* is used as manure.

P. Stable refuse does for that purpose.

M. Yes; but it contains insufficient nitrogen to produce a large crop. So we let the field have some more in the form of

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Chile saltpetre, and the additional expense is repaid by a correspondingly greater harvest.

P. But what if the Chilians refused to give us any more of their saltpetre?

M. They will send us as much as we wish and can pay for, because their's is a mountainous and almost uncultivated country. But unfortunately this source is beginning to give out.

P. Then what will the farmers use?

M. They will supply their fields with combined nitrogen in a different form. There is another, very widely distributed, compound of nitrogen, ammonia. We will treat of this substance in our next lesson.

19. AMMONIA.

M. Tell me something about nitric acid.

P. The sodium salt is found in Chile and is called Chile saltpetre. This is used as manure. Can we make gunpowder from it, also?

M. Not the ordinary black powder, but all varieties of smokeless powder. How do we prepare nitric acid from it?

P. By distillation with sulphuric acid. A liquid distills over which fumes in the air. I have some yellow stains on my finger; I cannot wash them off. Were they caused by the nitric acid?

M. Certainly. It forms a yellow substance on coming in contact with the skin. We must be very cautious with it, for it is strongly corrosive.—What is the formula for nitric acid?

P. HNO_3. So it contains a large proportion of oxygen, which it readily parts with. On this account it dissolves most metals, even those which are not soluble in other acids. During the solution yellow vapours are given off. These contain less oxygen than nitric acid.

M. What is the basicity of nitric acid?

P. Hm; I was not told that. But as it contains only one hydrogen it must be monobasic.

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M. Quite right. We now come to another nitrogen compound, ammonia. Do you know the name?

P. Yes. A friend once let me smell a bottle; it made my nose tingle and brought tears to my eyes; but I was told it was ammonia and very good for me.

M. It may have been ammonia, i.e., its solution in water. Ammonia is a compound of nitrogen and hydrogen. Under ordinary conditions it is a gas easily soluble in water in large quantities. The solution, which looks like water and smells strongly of ammonia, is usually called ammonia. Here is some. Smell it cautiously!

P. Yes. It is the same smell. How well we remember smells!

M. In ordinary life, such smells as these are not common; therefore you recall them just as you recollect the details of any unusual event. So the smell is a very valuable aid to the chemist in the recognition of various substances.

P. Yes; I see that. I can now, quite easily, recognize chlorine, hydrogen sulphide, and ammonia.

M. By using the nose we can detect extraordinarily small quantities. The nose is one of the most delicate of tests. (P. 132.)

P. What actually causes the smell?

M. It is almost certainly due to a chemical process. The substance which produces the smell is absorbed by the moist membrane inside the nose, and there acts on the nerves of smell by attacking them chemically. Therefore all substances which act chemically on organic compounds have strong smells. And since the organisms at the extremities of the nerves of smell are very small very minute quantities are sufficient to produce an appreciable effect. But we must return to our ammonia. The formula is NH_3. What does that imply?

P. That it consists of one combining weight of nitrogen and three of hydrogen.

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M. What is its molecular weight?

P. $14.04+3\times1.01=17.07$.

M. Right. So what do you conclude regarding its gas density? Is ammonia lighter or heavier than air?

P. Its gas density is a little more than half that of air. The quotient 17.07/28.90 is 0.59. So ammonia is considerably lighter than air.

M. Quite right. The molecular weight of any gas divided by 28.90 always shows how much heavier it is than air. If the quotient is smaller than one—

P. Then the gas is lighter.

M. Good. You deserve a reward, so I shall show you an experiment. Do you remember how we prepared nitrogen from saltpetre with iron (p. 158)? Well, we will make some hydrogen in a similar manner by heating iron with sodium hydrate. There is always an excess of water present in the latter, and this is decomposed by the iron. (I. p. 130.) I put the mixture (1 part of caustic soda to 5 parts of iron) in a test-tube, insert a cork fitted with a glass-tube burner, and heat. There; a gas is now coming off. Just apply a lighted match to it.

P. Yes; that is the hydrogen flame. What has this to do with ammonia?

M. I will show you that ammonia consists of nitrogen and hydrogen. To do this, I mix together 1 part of saltpetre, 2 parts of sodium hydrate, and 20 parts of iron; and apply heat in the same way as before. Just smell!

P. It smells of ammonia.

M. I dip a glass rod in concentrated hydrochloric acid and hold it at the mouth of the test-tube.

P. A dense cloud forms. What causes it?

M. You will see immediately. I hold a damp piece of litmus paper over the mouth—

P. It turns blue. Is there a base there?

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M. Yes. Just test the ammonia solution in the bottle with red litmus.

P. Yes; the paper became blue even before I had dipped it in. So ammonia is a base. But yet it does not contain a metal.

M. No. What constituent is essential in a base? (P. 49.)

P. Let me think. It was something similar to the acid hydrogen. Ah, yes; it was OH.

M. Yes. The hydroxyl, OH, is present in all bases.

P. But—ammonia is NH_3; there is no hydroxyl there.

M. Quite right. It is the same with ammonia as with sulphur dioxide and sulphur trioxide, which are not acids, but become such by uniting with water. In the same way ammonia is an anhydride and forms a base with water; thus:

$$NH_3 + H_2O = NH_4OH.$$

We call the NH_4 combination ammonium. Therefore NH_4OH is ammonium hydroxide and is a base like sodium hydroxide, NaOH.

P. Then is NH_4 also a metal, like sodium?

M. We have not yet succeeded in isolating this substance; but, still, what we know of it goes to show that ammonium actually is a combination of metals. You know that in nitric acid the combination NO_3', or the nitrate ion, behaves quite similarly to the elementary chlorine ion in hydrochloric acid. In the same way, there is an ammonium ion, $NH_4^{\cdot}$, which behaves alike in every respect to the potassium ion, $K^{\cdot}$.

P. Can ammonium form salts?

M. Certainly. The cloud which you saw just now was a salt of ammonium.

P. It was produced when you held some hydrochloric acid near.

M. Yes; hydrogen chloride and ammonia give ammonium chloride:

$$HCl + NH_3 = NH_4Cl.$$

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P. But this seems quite a different method of making a salt from those you previously described to me. (P. 88.)

M. You remember that when a salt was formed from an acid and a base water was produced each time.

P. Yes; that is just where the difference lies.

M. Well, ammonia gas is the anhydride of the base ammonium hydroxide: $NH_4OH - H_2O = NH_3$. It is the base minus water. When this anhydride comes in contact with an acid, it can only form the salt, without the water:

$$NH_3 + HCl = NH_4Cl.$$

P. Ah; is that how it is? Let me think it over for a little. Yes; now I understand. Again, it is quite simple.

M. We can, therefore, take a solution of ammonia if we wish to use a base; and in future we shall often have occasion to do so.

P. Can we not obtain the hydroxide by evaporation, as in the case of sodium hydrate?

M. No; that does not work; for it splits up again into ammonia and water, and both are volatile. The ammonia is given off first. It is the case of the sulphur dioxide (p. 139) over again.

P. Ah, that's why the solution smells so strongly.

M. Quite right. What do you suppose? Is ammonia combustible?

P. It should be, on account of the hydrogen in it, but nitrogen is not combustible.

M. If we try to set alight to a current of ammonia gas it burns so long as we hold a flame to it, but it goes out when the flame is removed. However, by the aid of an accelerator, such as platinum, we can burn a mixture of ammonia and air. In this case, nitric acid is produced.

P. Then that will be the way to make nitric acid, should the Chile saltpetre ever be all finished. How would that do?

M. Quite well, if we had enough ammonia.

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P. How do we obtain ammonia?

M. It is now principally got from coal. This, on being heated in closed retorts, gives off a quantity of gas which is used for lighting purposes.

P. Is that what they make in the gas-works outside the town?

M. Yes. The gas contains ammonia as well as many other substances. This collects in the liquid portion of the distillate, called the "gas-liquor." The ammonia is distilled over, and either obtained as a concentrated solution in water or converted into a salt.

P. Then how does the ammonia get into the coal-gas?

M. Coal contains nitrogen, and a portion is changed into ammonia by the heating. Just the same process takes place in the coke-ovens.

P. What are they for?

M. In smelting iron we have to use not ordinary coal but the purer carbon which is left after coal has been heated. This residue is called coke, and the heating process is exactly the same as for the preparation of coal-gas. They used formerly to let the gas escape or burn away, because it was not suitable for giving light. But now they use it for driving large gas-engines, and can thus afford to remove from it a valuable quantity of ammonia.

P. You have told me a great deal about ammonia, but I have not yet actually seen any. Can you show me some?

M. No, I cannot; because it is a colourless gas. If I warm a concentrated solution in water, first of all ammonia, with almost no water, escapes; the liquid appears to boil although the temperature is quite low. The bubbling is caused by the ammonia.

P. To be sure, there is not much to see, but plenty to smell.

M. We can liquefy ammonia pretty easily by cooling, and increasing the pressure. Therefore we can store it, like chlorine, for transport in steel bombs. The liquid is colourless, like water.

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20. PHOSPHORUS.

M. To-day we shall study phosphorus.

P. Hurrah; I am very glad. This appears to me a much more wonderful substance than the others, because it shines in the dark.

M. Those who first found phosphorus also thought so. The story of its discovery is rather curious.

P. Please tell me about it.

M. You know that in early times chemistry was pursued in the hope that gold could be produced from substances of trifling value.

P. Yes; those were the days of the alchemists.

M. Well, in the year 1670, there was one of these alchemists, a merchant who had failed, called Brandt. He considered that man was the noblest of nature's creations, and that if we could make gold of anything it must be from something which has passed through the human body. So he took our urine, evaporated it to dryness, and distilled the residue over a hot fire in a clay retort. He obtained not gold, but phosphorus.

P. How did he manage that?

M. Human food contains oxygen compounds of phosphorus which pass out in the excreta. They become reduced by the organic bodies present there, and the phosphorus is set free. We, of course, only obtain a very little, but its properties are so striking that we can easily detect them.

P. And so Brandt did not get any gold.

M. His phosphorus was nearly as valuable, for he went round exhibiting it as gold, and sold some small quantities at a very high price.

P. Why did not other people also make phosphorus, since everyone had what was necessary for that purpose?

M. Brandt told no one how he obtained his; for he worked not in the interests of scientific research, but for his own pocket. However, this did not last long; for others found out

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how to make it, especially a German scientist, named Kunckel, and an Irishman, called Boyle—

P. The same man who invented Boyle's law?

M. Yes. Both gave accounts of how they had prepared phosphorus; and since then we have discovered rich sources of this element, so that to-day it is not very dear. I have some here as it is sold in the shops in the form of cylindrical rods which look like white wax when pure.

P. Are they crystalline?

M. No; we pour rod-phosphorus into moulds, as we prepare sulphur. It melts very easily. I take some out of the bottle—

P. Then what is that liquid? Is it water?

M. Yes. We keep phosphorus under water, so that it may not ignite in the oxygen of the air. Therefore I immediately place the rod in a dish of water, and keeping it there cut off a piece.

P. It is also soft, like wax.

M. Yes. Now I put it into a test-tube with some water, and heat cautiously.

P. There; it has melted already. What is that kind of white smoke on the surface?

M. Phosphorus melts at 44°. The white cloud is caused by a small quantity evaporating through the water and becoming oxidized. The product of the combustion is not volatile, and, therefore, condenses in a cloud. I place the tube containing the melted phosphorus in cold water. It has now become quite cold, but the phosphorus is still liquid.

P. How can that be? The solidifying and melting temperature must be the same.

M. It is a case of supercooling. (I. p. 165.) If I rub a glass rod on some solid phosphorus and touch the supercooled liquid with it, solidification immediately ensues (as happened with the ice), for I have dipped in a trace of solid phosphorus.

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P. That was a pretty experiment! May I try it?

M. I would rather you did it with a less dangerous substance. We will now subject the phosphorus to greater heat.

P. Will it not burn then?

M. Certainly; but no matter if it does. I carefully dry a piece (the size of a pea) with filter-paper, place it in a dry test-tube, stop up the mouth loosely with some twisted wadding, and warm cautiously.

P. There is a greenish flame inside.

M. The phosphorus is consuming the small quantity of oxygen there. Now nitrogen only is left, and I can gradually increase the heat. Tell me what you see.

P. The liquid phosphorus was clear at first; now it is red and clouded. It looks as if some red solid had deposited. What can it be?

M. It is another form of phosphorus, which, as in the carbon and sulphur instances, is allotropic. The white variety changes into the red on heating. Were I to continue the experiment for a sufficient time the whole contents would be converted. But that would take too long. Here is a supply of red phosphorus in this bottle.

P. But this is not immersed in water.

M. It is not necessary; for red phosphorus oxidizes so very slowly in the air that we need take no special precautions. You can see that this really is phosphorus, because it burns in the same way as the white; and, in doing so, likewise gives off a thick white cloud. I set a light to a small stick of white phosphorus—

P. It does not burn nearly so brightly as it did in oxygen!

M. I see, you have not forgotten that experiment. Now I hold some red phosphorus over the burner on a strip of tin—

P. It is much more difficult to burn.

M. Quite so. I can show you this difference much more clearly. I have here a thick sheet of tin. I lay it on the tripod. On one corner I place a piece of white, on the other

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a little heap of red, phosphorus. Now I put the burner under the centre so that it heats each variety equally.

P. The white phosphorus is burning already!

M. And you will have to wait a long time before the red burns. In the mean time we will look at something else. Let us change some red back into white. To do this I treat it in the same way as I did the white, only I heat more strongly. What do you see?

P. Transparent drops, like oil, form on the upper part of the tube. Some are now turning red.

M. The red phosphorus has changed into vapour, which has condensed as liquid white phosphorus. Where the heat is somewhat greater this variety has partly changed back again into the red.

P. I cannot understand this: on heating, the white first changes into red, and then the red changes again into the white!

M. It is not easy to understand. The fact is that white phosphorus is unstable; red is stable, and that through the whole range of temperature up to its boiling-point. Only, at the ordinary temperature, the white is converted into the red very (imperceptibly) slowly. On raising the temperature the reaction goes faster; and, therefore, you saw the white phosphorus change into the red when heat was applied.

P. Good; now I understand. But how is the white produced again from the red?

M. The white is formed only from the vapour. I heated the red phosphorus until it had changed into vapour; this condensed as white phosphorus; and, therefore, it is as such that we always obtain it by preparation from its oxygen compounds.

P. But if the red is more stable it, and not the white, must be formed.

M. No. According to one of the laws of nature, in every reaction the more unstable form is always produced first;

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then it depends on the prevailing circumstances whether this changes into the more stable variety. (P. 105.)

P. I would like to get a better idea of this.

M. This small apparatus here will show you another instance. It is a small retort (Fig. 24) in which some water

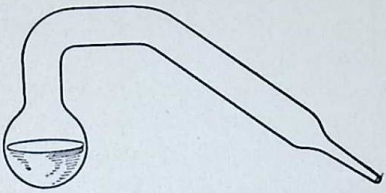

FIG. 24.

is enclosed in a vacuum.

P. How did you manage that?

M. Quite easily. You draw out the tube to a fine point, boil the water, and when all the air has been expelled by the steam you melt the sides of the orifice together. You can try it yourself next time. Now, I make a freezing mixture with ice and salt. The thermometer stands at $-5°$. I dip the neck of my retort, which is full of water-vapour, into it. What will happen?

P. The vapour will be condensed, and must form ice.

M. Look what has formed.

P. It is water. Has it supercooled?

M. Certainly. You see, although liquid water at $-5°$ is much more unstable than ice, yet it is produced first; just as the more unstable white phosphorus was formed, first of all, from the vapour.

P. Please, tell me, why does phosphorus shine in the dark?

M. Because it is burning.

P. But it looks quite different when it burns; it has a bright flame then.

M. That is a quick combustion. When it lies in the air at the ordinary temperature it burns slowly, and in doing so

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produces different substances from those formed by the quick burning.

P. Then does the surface shine because it is hot? The light appears greenish.

M. No; the surface is not hot. You know that light is a kind of energy. When phosphorus burns, whether quickly or slowly, energy is set free; and during the slow burning in the cold a portion changes into light.

P. I do not yet quite understand.

M. We obtain most of our light from hot substances; for when the temperature of a body rises above 540° it begins to emit a part of its heat as light. This, at first, is principally red. As the temperature rises the light becomes whiter, until eventually it is quite white. Therefore, we describe a temperature of 500° to 600° as red-hot, that of 800° as yellow-hot, and a still greater heat as white-hot.

P. Does this apply to all substances?

M. To most solids; gases are exceptions. This appearance of light, which depends on the temperature, we call temperature light. There are, in addition, other kinds, which owe their effect to other (for instance, to chemical) forms of energy. The light from phosphorus is an example of chemical energy; and, in such cases, the different varieties depend on circumstances; for instance, phosphorus produces a greenish light.

P. And glow-worms?

M. They also give a greenish light which is not a temperature light, but most probably a chemical effect.

P. Perhaps they can make phosphorus?

M. No; we have proved that their light does not come from phosphorus. This is very poisonous and would destroy the animal. It is only the white, not the red form, which gives light.

P. Why is that?

M. I have already told you that the latter does not oxidize in

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the air to any appreciable extent. Consequently it cannot give light, because no energy is liberated. This is also why red phosphorus is not poisonous. Now let us turn to what is produced when phosphorus burns.

P. It is, of course, an oxide of phosphorus.

M. Certainly. There are several oxides; but we will only study the one with the highest proportion of oxygen. This is formed when phosphorus burns with a bright flame. I place a small basin containing a little phosphorus on a plate of glass; set it alight; and cover it with a large, dry, inverted beaker.

P. How pretty! It is like a miniature snow-storm.

M. The phosphorus burns, forming an oxide with the formula P_2O_5, called phosphorus pentoxide. Penta is the Greek for 5. It is a snow-white substance which, like snow, can be squeezed into balls. I quickly gather up some, which has fallen on the glass plate, and throw it into water.

P. It hisses.

M. Phosphorus pentoxide attracts water with great eagerness and gives off a large quantity of heat; this produces the hissing. It is, therefore, a very efficacious desiccator. Anything damp shut up with it loses all trace of water; and air led over it becomes dry at once. Just test the solution with litmus.

P. The paper turns red; so an acid has been formed. Let me think; the pentoxide must have united, as the sulphur trioxide did, with the water; perhaps in this way: $P_2O_5 + H_2O = H_2P_2O_6$?

M. You are right in the main point; but in this case the equation is somewhat more complicated. It should read:

$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

The acid produced is called phosphoric acid; it is tribasic. However, in point of fact, a monobasic acid is first formed, according to the equation:

$$P_2O_5 + H_2O = 2HPO_3.$$

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But this is unstable, and soon turns into the tribasic compound by asborbing water:

$$HPO_3 + H_2O = H_3PO_4.$$

We will only trouble ourselves about the latter. How many kinds of salts will it be able to form?

P. Three, if it is tribasic. Either one, two, or all three of the hydrogen can be replaced by a metal.

M. Quite right. So phosphoric acid can have three kinds of phosphate ions, namely, the trivalent PO_4''', the divalent HPO_4'', and the monovalent H_2PO_4'. These damp crystals here are phosphoric acid; they are very easily soluble in water, and are, therefore, difficult to obtain dry. Their solution in water has a clean, pleasantly sour taste. Try it!

P. But phosphorus is poisonous.

M. It is; but phosphoric acid is not. Compounds of this acid are, indeed, indispensable constituents of all living organisms. Look; here is the calcium salt of phosphoric acid.

P. That is a bone!

M. It was once; but it has been burned. Bones consist of calcium phosphate and an organic substance which, on boiling, yields gelatine. If roasted strongly in the air the organic matter burns away and the calcium phosphate remains behind. We call this residue *bone-ashes*. Compounds of phosphorus are also found in the tissues of the body, especially in the nerves and brain. Moreover, plants require phosphates for their development, and we have to spread the fields with a fresh supply when they become exhausted.

P. Where do they come from?

M. Ordinary stable manure contains phosphates. Besides, calcium phosphate, a mineral, is found in many places; it goes by the name of *phosphorite*. The dross, also, from the purification of iron ores, which often contain a little phosphorus, consists principally of calcium and magnesium phos-

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phates. This dross is used in large quantities for agricultural purposes.

P. I have several times seen superphosphates advertised in the papers as a manure. Is this something of the same nature?

M. It is a substance which is prepared by the action of sulphuric acid on phosphorite, in order to make the phosphoric acid more soluble and accessible to the plants. But we will have more to say about this, later on, when dealing with calcium. We shall here leave phosphorus.

P. Has it no more compounds?

M. Indeed, it has; very many more. But we will not study them now lest you become confused by too many new names.

21. CARBON I.

M. To-day we come to carbon. You already know a great deal about it.

P. Yes. It has three allotropic forms; diamond, graphite, and amorphous charcoal. The coal found in nature—anthracite, bituminous coal, bore coal, etc.—is not pure carbon.

M. What does it contain besides carbon?

P. An ash, and also some nitrogen.

M. Another important constituent of all coal is hydrogen. The illuminating-gas obtained from it contains hydrogen and compounds of hydrogen and carbon; therefore, those elements must have been present in the coal. What carbon compounds do you know?

P. Carbon monoxide and carbon dioxide. Both are gases; the first is poisonous, the second is not.

M. And what is carbonic acid?

P. Carbonic acid is formed by the combination of carbon dioxide with water. It is a weak acid, and is only known as a solution in water. If we try to obtain it pure it splits up again into carbon dioxide and water.

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M. Yes. So carbon dioxide is, therefore, the anhydride of carbonic acid. Write the formulæ!

P. Carbon monoxide is CO; carbon dioxide is CO_2; carbonic acid is H_2CO_3, therefore it is dibasic.

M. Right. Why is carbon of special importance?

P. Because it is present in all forms of life. Besides, it is interesting on account of its energy.

M. Explain yourself more clearly!

P. By the combustion of carbon we obtain heat, power to do work, light, and all other kinds of energy. Carbon receives its energy from the sun, because plants produce carbon from carbon dioxide by the aid of sunlight.

M. They do not produce carbon, but compounds of carbon which are combustible, and therefore contain no (or, at any rate, insufficient) oxygen to burn up the carbon present in them. We will enter a little deeper into this subject. And first let us answer the question, how do we measure energy?

P. Energy appears in many very different forms; so we must have a special standard of measurement for each.

M. That is what we used to have. But we now know of the law of the conservation of energy. If we choose a definite quantity of any one kind as a unit we can use this same unit for every other form, provided that we know how much of any other energy is equivalent to our unit.

P. An example, please.

M. Work, for instance, was formerly estimated by the product of the weight and the height to which it was lifted. The weight was the kilogram, the height was measured in meters, and the unit of work was called the kilogram-metre. On the other hand, heat used to be reckoned in calories (I. p. 169); i.e., the unit was the amount of heat necessary to raise the temperature of one gram of water through one degree. Then, when we came to find out that work and heat were interchangeable into each other we compared the

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two units by converting so many kilogram-metres into calories; and thus discovered that 0.427 kgm. equal 1 cal.

P. I understand.

M. But afterwards we met with still other forms, electrical energy, energy of motion, etc. If each were measured by a different standard we would have to make very many various comparisons, since every form would have to be judged in its relation to each of the others. Two varieties of energy require only one equation; three require three; four require six; five require ten; etc.

P. How do you get those figures?

M. These are the numbers of different pairs possible, supposing we had two, three, etc., standards. It is evident that we can do away with all these calculations if we choose the standard unit so that every variety of energy can be measured by it. I see you do not yet quite understand. If we measured work, not by the kilogram-metre, but by 0.427 times that quantity, that would make one calorie also the unit of work, and any number of calories would show the same number of work-units, and vice versa.

P. Yes; now I see. So we must leave one standard as it is and make those for all the other forms of energy correspond.

M. They preferred to introduce an entirely new standard. I will not explain to-day how they made their choice. They fixed on a unit which is pretty nearly, only 1/10 less than, 10 kgm. It is called the joule.

P. What a peculiar name!

M. Joule was an English physicist. To him we owe the first accurate measurements regarding the relation between the units of heat and work. He was one of the first to admit the law of the conservation of energy (1843). This had been discovered a short time before, in the year 1842, by a German physician, Julius Robert Mayer. One calorie is equal to 4.18 joules; and, therefore, 1 joule represents 0.239 cal. So, in future we shall measure quantities of heat in joules;

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but you must take note of the above proportion because we often find heat still estimated in calories.

P. Why have you gone into this question in such detail?

M. Because it is the basis of all scientific measurement. Besides, we are just about to put the subject of my remarks to a direct application. The heat of combustion of carbon is 406,000 joules, or 406 kilojoules; for 1000 joules are called one kilojoule, just as 1000 g. represent one kilogram. The symbols are j. and kj.

P. I do not understand this at all.

M. I am not surprised. Let us study the question bit by bit. To begin with, you know that heat is produced when carbon burns.

P. Yes; for ovens are heated with charcoal.

M. Very well. Obviously, the more charcoal we burn the greater is the amount of heat we obtain; in fact, the latter is proportional to the weight of charcoal consumed. So if we know how much heat 1 g. of carbon gives we can calculate the product of any given number of grams.

P. Yes; but do we not have to take into account how the carbon is burnt? My mother always says that if a fireplace is not properly made the room will never be warm however many coals we use.

M. That's quite true; because with an ill-constructed grate the heat does not enter the room but escapes up the chimney. But if we collect all of it we find that a definite quantity of carbon always gives a fixed amount of heat.

P. Is this a new law of nature?

M. You can consider it as a special instance of an old one. Each substance has, as you know, certain definite properties; the heat of combustion is a property, and therefore must have a constant value.

P. I would never have dared to draw such a conclusion.

M. It is a good thing for us to work out conclusions; but we must see they are proven. This theory of the heat of

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combustion has been very often carefully tested and found to be correct. It is a necessary result of the conservation of energy. Let us consider this subject more fully. Burning is only one form of chemical action, but our theory applies to all. If any substance whatsoever undergoes a chemical change a definite quantity of heat, proportional to the weights of the reagents, is produced or absorbed.

P. Can you explain this a little more clearly?

M. You know that during chemical changes the energy of a substance alters. Well, this variation appears as the heat which we observe during the reaction.

P. But it could appear, also, as other forms of energy.

M. Certainly; and we have less heat if we have these other varieties. But they only occur when we make special arrangements. If we simply let substances react the whole of the energy appears as heat; and, therefore, it is as such that we can most conveniently measure the alterations of energy in chemical processes.

P. I think I understand you, but I am still not quite sure.

M. Let us take some examples. If I burn 1 kg. of pure carbon under a kettle containing 1000 kg. of water its temperature rises 8.10°. So how many calories does 1 g. of carbon produce? Let us calculate it. 1000 kg. of water equals 1,000,000 g.; each gram has become warmer by 8.10°; so the total heat equals 8,100,000 cal.

P. I understand.

M. These 8,100,000 cal. have been produced by 1 kg., or 1000 g., of carbon; consequently 1 g. of carbon yields 8100 cal.

P. Yes; that is quite simple.

M. Well then; 1 cal. represents 4.18 j.; therefore, 1 g. of carbon supplies 33860. j. But it is better to state the heat of reaction, not of 1 g., but of so many grams as the combining weight has units. This, in the case of carbon is 12 g. which yields 406,000 j. or 406 kj. We call this number the heat of combustion of carbon. The last figures are represented

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by naughts, because we cannot measure correctly to fractions of a kilojoule.

P. Why is it better to use 12 g. as the basis?

M. I am just going to show you. Write down the combustion of carbon as a chemical equation. With what does the carbon unite?

P. With oxygen. The equation is $C+2O=CO_2$.

M. This shows you, as you know, the weight of the reacting substances. But if I write $C+2O=CO_2+406$ kj. it tells me the amount of energy, also. It will then read thus: the sum of the energy of 12 g. of carbon and 32 g. of oxygen equals the energy of 44 g. of carbon dioxide plus 406 kj. In order to write such an equation as this we must always express the production of heat in terms of the number of combining weight units of grams.

P. I cannot contradict you on any point, but it seems a bold thing to calculate the energy literally like this.

M. Perhaps that is because the separate amounts of energy are not, and never can be, known. What we have estimated is the variation of energy; that is all the equation shows. For you can twist it about as you please; you never obtain a positive, but always a comparative, value for the energy of any individual substance. This, however, we can measure.

P. I quite see that everything is as you say; but it is somewhat difficult for me to get the hang, as it were, of all these new ideas.

22. CARBON II.

M. What you learned yesterday forms the basis of a separate science, the study of the heat of chemical reactions or thermochemistry. For every chemical process can be examined in the same way as we tested the combination of carbon with oxygen, and in each case we obtain the same sort of equation concerning the proportions of energy present. Tell me what you remember about it.

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P. I recollect the last part best. Chemical equations can also express the energies of the reacting substances, but we do not know the positive amount, and can only make a comparison before and after the process.

M. And that is the most essential thing to know, as I will show you, if we study this question somewhat more closely. You know that carbon can form two different compounds with oxygen. So we ought to be able to define the variation of energy when carbon changes into carbon monoxide.

P. Yes; all we have to do is simply to burn some carbon to carbon monoxide and estimate the heat produced.

M. Ah; if we can! But carbon only burns to the dioxide, and we know no simple means of converting it directly into the monoxide. All we can do is to burn the monoxide to the dioxide. We then obtain 284 kj., and, therefore, the equation is:

$$CO + O = CO_2 + 284 \text{ kj.}$$

P. But I do not see how that helps us.

M. Let us make a simple calculation. Write down our first equation and the last one underneath it, then subtract; you can cancel the equivalent factors.

P.

$$\begin{array}{r} C + 2O = CO_2 + 406 \text{ kj.} \\ \underline{CO + \ O = CO_2 + 284 \text{ kj.}} \\ C + O - CO = 122 \text{ kj.} \end{array}$$

M. Now bring the negative factor over to the other side.

P. $C + O = CO + 122$ kj.

M. There, you have what you wanted. The equation says: the energy of carbon and oxygen equals that of carbon monoxide plus 122 kj. That represents the combustion of carbon to carbon monoxide.

P. The calculation appears to be correct, but I cannot follow it.

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M. Since we are able to estimate amounts of energy we can also add and subtract them as measurable quantities; therefore, so far as that part goes, the calculation is, without doubt, correct and admissible. I will make clear to you by a diagram just how we get our result. The line *AB* (Fig. 25)

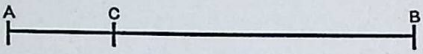

FIG. 25.

represents the heat produced when carbon burns to carbon dioxide. Well, let us suppose that the combustion takes place in two stages; first to carbon monoxide, then from this to carbon dioxide. The first stage extends from *A* to *C*, the second from *C* to *B*. Now we have been able to measure the distances *AB*, and *CB*, which represents the burning of carbon monoxide to the dioxide. Consequently, we can also calculate the unknown length *AC* by simply subtracting *CB* from *AB*.

P. I now understand. It is really very simple. I am vexed that I did not see it at once.

M. It is often the case, as you already know, that the simplest thing is just what seems the most difficult. We will be content, for the mean time, with this glance into thermochemistry. We have now to study certain of the carbon and hydrogen compounds. The first is marsh-gas. Next time you go into the wood you can bring home a bottle full of it, like the one I have here.

P. Is there a gas manufactory in the wood?

M. Yes; in every marsh. Surely you have noticed bubbles rising from time to time from the bottom of a swampy pool. If we stir the dead leaves with a stick a fairly large quantity of gas escapes. We can easily collect some by filling a bottle with water, immersing it mouth downwards under the surface of the bog, and letting the bubbles rise into it, prefer-

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ably through a funnel which will catch them more readily (Fig. 26). This gas consists of a mixture of marsh-gas and carbon dioxide. We can remove the latter with some sodium hydrate solution and obtain the marsh-gas fairly pure.

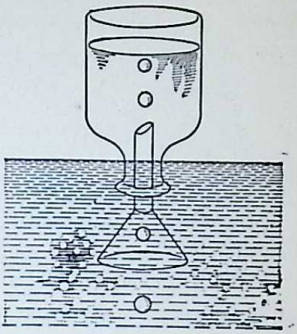

FIG. 26.

P. How do we recognize it?

M. It is colourless, is composed of carbon and hydrogen, and has the formula CH_4. Its molecular weight is therefore—?

P. C=12; 4H=4.04; the total=16.04. So it is lighter than air, whose corresponding density figure is 28.90.

M. Right. Will it burn?

P. I should say so, for it is composed of two combustible elements.

M. We will make sure. I let some rise into a test-tube, and set it alight (after fitting the bottle, while inverted under water, with a cork through which pass two tubes closed by pinch-cocks). (Fig. 27.)

P. It burns with a pale flame, something like hydrogen does. How does it get into the swamp?

M. It is formed from decaying leaves. No oxygen from the air can reach them there, so their carbon decomposes the water and gives carbon dioxide and marsh-gas.

$$2C + 2H_2O = CH_4 + CO_2.$$

To prove to you that it consists of hydrogen and carbon we will fix our pointed burner (I. p. 145, Fig. 27) on to the exit tube and let the gas burn under a large, dry beaker. This becomes dim with drops of moisture; and if I afterwards shake these up with a little lime-water we obtain a precipitate of calcium carbonate.

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P. Yes; it is as you said.

M. Marsh-gas is a constituent of illuminating-gas, for it is produced when coal is heated. It is also often found shut up in coal seams, where it is probably formed in the same manner as in the marshes. Then, when the coal is

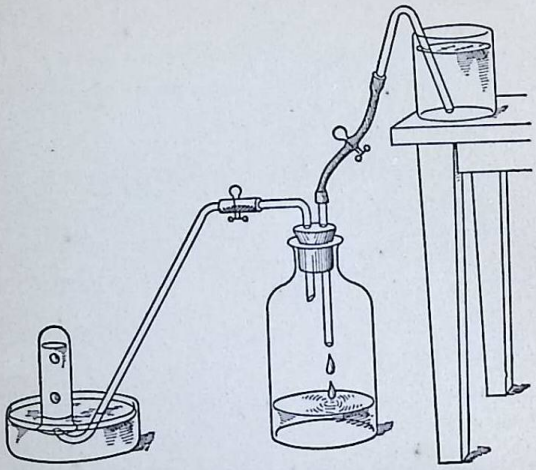

FIG. 27.

mined, it streams out into the pit and is known as fire-damp, a dreaded enemy of the miners.

P. Is it poisonous?

M. No; although it will not support life. But it forms an explosive mixture with air, and if this ignites at the miner's lamp, a dangerous explosion results. Since it is without smell, its presence is not easily detected. Write down the equation for the combustion of marsh-gas.

P. One carbon requires two oxygen; four hydrogen also require two oxygen; so we need, altogether, four oxygen:

$$CH_4+4O=CO_2+2H_2O.$$

M. Very good; only I would rather have the molecular formulæ $CH_4+2O_2=CO_2+2H_2O$; 1 volume of marsh-gas

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requires 2 of oxygen. How many volumes of air does 1 of marsh-gas need?

P. 1 volume of oxygen is contained in 5 of air; so the answer is 10 volumes of air.

M. You see, a relatively small amount of fire-damp gives a large quantity of the explosive mixture. Great heat, 886 kj., is developed when marsh-gas burns. Now the carbon gives 406 kj., four combining weights of hydrogen yield 572 kj., and their sum is 978 kj.. So when we burn marsh-gas we obtain 92 kj. less heat than if we had ignited the same quantity of carbon and hydrogen separately.

P. How can that be? Surely just the same amount of heat ought to be produced.

M. That is what we used to think; but we were wrong. Just consider: you first take the two elements and make them combine to form marsh-gas, which you then burn. If these constituents and their product ought to yield the same quantity of heat, then no energy must be required for the formation of marsh-gas from its elements.

P. Now I understand. It is the carbon monoxide and dioxide case over again.

M. Yes; and by applying that example we can calculate what heat is developed when marsh-gas is formed from carbon and hydrogen. For we have

$$C + O_2 = CO_2 + 406 \text{ kj.}$$
$$2H_2 + O_2 = 2H_2O + 572 \text{ kj.}$$
$$CH_4 + 2O_2 = CO_2 + 2H_2O + 886 \text{ kj.}$$

If you subtract the third equation from the sum of the first two you obtain

$$C + 2H_2 = CH_4 + 92 \text{ kj;}$$

in other words, carbon and hydrogen give marsh-gas plus 92 kj. Therefore, since the elements have used up a portion

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of their energy on combining, when we come to burn the compound, we obtain so much the less heat.

P. I see this quite clearly; the diagram on p. 186 has helped me to grasp your meaning.

M. Marsh-gas is taken as the starting point of *organic chemistry*. You have already heard this name (I. p. 227). To what does it relate?

P. To an enormous number of carbon compounds, many of which are to be found in living organisms.

M. Yes. Nearly all these substances contain hydrogen, and, therefore, we have chosen the hydrocarbons as the simplest types to serve as a basis for the classification and arrangement of the others.

P. Are there many hydrocarbon compounds?

M. Yes; very many. Those directly allied to marsh-gas have the following composition: CH_4; C_2H_6; C_3H_8; C_4H_{10}; C_5H_{12}; etc.

P. An addition of one C and 2H in each case. Then where is this series found?

M. In crude petroleum. You know that this is found in the ground in America, in the Caucasus, and also, quite recently, in Germany. The first members of the group are gases. They become less volatile the more carbon they contain; so, as we mount the series, we find liquids, and then solids. When we tap a petroleum spring the gases are first given off. In Pennsylvania these natural supplies are collected and burnt to provide heat for all sorts of industrial purposes.

P. How very convenient.

M. Those from C_5H_{12} upwards are liquid; the more C they contain, the higher is their boiling-point. Those from C_5H_{12} to C_8H_{18} are easily volatile and very inflammable, and so cannot be burnt in lamps on account of danger from fire. They come on to the market as *petrol*, which is used to drive engines, especially those of motor-cars.

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P. Yes; I have often heard motorists mention the name.

M. Those from C_8H_{18} upwards are sold as ordinary illuminating petroleum, or kerosene. Then we come to some richer in carbon; these, being viscous, are used as lubricating oils. The still higher members, which are half solid, you meet with as vaseline; and, finally, those completely solid are the paraffin waxes, which you know in the form of candles. The latter product has given its name to the whole of this series, and marsh-gas is the first member of the paraffin group.

P. I need not learn all those compounds by heart, need I?

M. No; that is not at all necessary. We do not know many of them in the pure state, because they are always found as complex mixtures and have such similar properties that we can only isolate them with great difficulty.—But this is by no means the only group of hydrocarbons. We obtain another, quite different in composition, from the coal-tar from the gas-works. The first member has the formula C_6H_6, and is called benzene.

P. Is that the same as benzine?

M. No; you must be careful not to confuse the two. Benzene is a water-clear liquid which boils at 80° and solidifies at 5°. It is, of course, inflammable. I set fire to some. You see, a quantity of soot is deposited from the flame, due to the large proportion of carbon present. I show you this substance because it also is of great importance. It is the basis of many of the artificial colouring-matters. The so-called aniline or coal-tar dyes are derived from benzene and its homologues.

P. Then they form a group similar to the marsh-gas series?

M. Yes; the various members are C_6H_6; C_7H_8; C_8H_{10}; etc. Here again each successive compound adds on CH_2. But this is not such a long series.

P. Now I begin to see the vast extent of organic chemistry.

M. I will just mention one other hydrocarbon which is

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also obtained from coal-tar. It is naphthalene, $C_{10}H_8$. Here is some. It forms glossy, white crystals and has a strong smell.

P. Ah; I have seen this before; my mother uses it to keep moths away.

M. Quite right. Naphthalene contains still more carbon than benzene does. Therefore it forms a tremendous black deposit on burning. Just look here!

P. The soot is flying about like snow-flakes.

M. So much for the hydrocarbons themselves. In order to give you some slight idea of what we mean by their derivatives let me show you this substance. It is a heavy, colourless liquid. Do you recognize the smell?

P. It reminds me of a sick-room. I do not know what it is.

M. It is chloroform. If we inhale its vapour for a short time we become unconscious and can then undergo the most painful operations without feeling anything. It is a derivative of marsh-gas and has the formula $CHCl_3$.

P. That tells me it contains chlorine. But what has it to do with marsh-gas?

M. If I write the two formulæ thus:

$$\begin{matrix} & H & \\ & H & \\ C & & \text{and} \\ & H & \\ & H & \end{matrix} \qquad \begin{matrix} & H & \\ & Cl & \\ C & & \\ & Cl & \\ & Cl & \end{matrix}$$

you see that chloroform is formed from marsh-gas by replacing three hydrogen with chlorine.

P. Then can we make it that way?

M. Certainly. If we bring the two gases in contact they react according to the equation:

$$CH_4 + 3Cl_2 = CHCl_3 + 3HCl.$$

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And so we say that chlorine is substituted for the hydrogen, and, therefore, chloroform is a *substitution product* of marsh-gas. In the same way we can replace the hydrogen of any of the hydrocarbons with other elements, and even with groups of elements. So you can imagine what an enormously large number of these different products there must be.

P. I am glad I do not have to learn organic chemistry.

M. You are not yet far enough advanced; you will find, later on, that it is a very interesting subject. Now let us look at some more carbon compounds which do not, in a strict sense, belong to organic chemistry. This liquid here has the formula CS_2, and is called carbon disulphide.

P. What causes those lovely colours? The liquid itself appears to be colourless.

M. Carbon disulphide has the same effect as a glass prism in completely breaking up and separating light. I pour some out. It is most inflammable, and therefore somewhat dangerous. What will be produced when it burns?

P. The sulphur will give sulphur dioxide; the carbon, carbon dioxide. Is that right?

M. Yes. The heat of combustion is 1120 kj. Just calculate for me the heat involved in its formation. To do this you require to know the heat of combustion of sulphur; it is 297 kj. for one S, or 32.06 g.

P.

$$C + O_2 = CO_2 \qquad +406 \text{ kj.}$$
$$2S + 2O_2 = 2SO_2 \qquad +594 \text{ kj.}$$
$$CS_2 + 3O_2 = CO_2 + 2SO_2 + 1120 \text{ kj.}$$

consequently $C + 2S = CS_2 \qquad -120$ kj.

So 120 kj. are produced.

M. Wrong.

P. I have gone over my figures again and can find no mistake.

M. The number is right, but you have not read the sign correctly. The equation runs thus: the energy of carbon

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and sulphur equals that of carbon disulphide less 120 kj.; in other words, carbon disulphide has so much more energy than its elements; and, during its formation heat is not produced but absorbed.

P. Then a cooling effect must result from this reaction. Is such a thing possible?

M. Certainly. If, for example, a salt dissolves in water, the temperature nearly always falls. Carbon disulphide is formed, if we lead sulphur-gas over red-hot carbon; but in order to keep the reaction going we have to supply heat continually.

P. What do they do with carbon disulphide?

M. It is used for many purposes. It is a powerful solvent. Iodine disappears at once in it, forming a beautiful violet-red solution. Sulphur also easily dissolves, and after evaporation remains behind in isolated crystals. Fats and resins are acted on in the same way; so we can extract them from mixtures by dissolving them out with carbon disulphide. Again, it is an effectual remedy against the vine-pest which does so much damage to the vineyards. It kills these insects.

P. It seems to have a great variety of uses.

M. And those I have mentioned are by no means all. Just observe that carbon disulphide and carbon dioxide have nearly similar formulæ, CS_2 and CO_2. You will notice as we go along that compounds of oxygen and sulphur have analogous compositions; this is especially the case with their metallic compounds.—I will now show you another very remarkable substance, prussic acid.

P. It is a liquid, like water. Why is it sealed up in a glass tube?

M. Because it is exceedingly poisonous and easily volatile. If it were in an ordinary glass and you were to smell it you would immediately fall down insensible and might probably die.

P. It is as well to know that.

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M. Its formula is HCN; so it is similar to hydrochloric acid; only instead of chlorine it contains the carbon and nitrogen compound, CN. This is called the cyanogen group, and therefore prussic acid is hydrogen cyanide.

P. How did it come to be called prussic acid?

M. Because it was first prepared from prussian blue, a compound containing iron, which you will learn about later on.

P. Can we produce cyanogen by itself?

M. Yes; by heating its mercury salt. This decomposes, like the mercuric oxide, into the metal and cyanogen which is a gas, like chlorine, only colourless. Its molecular weight is 52, so the formula must be $(CN)_2$.

P. In this it also resembles chlorine.

M. Yes. Hydrogen cyanide forms salts containing the monovalent cyanogen ion, CN′. This white solid, potassium cyanide, KCN, is the best known. It, likewise, is very poisonous.

P. Yet you keep it in an ordinary bottle.

M. It is not volatile, and therefore has no smell. Just try.

P. But I do smell something; rather like bitter almonds! How can that be since it does not volatilize?

M. What you smelled was not potassium cyanide but prussic acid. This is an extremely weak acid, and therefore its potassium salt is slightly decomposed even by the carbonic acid in the air. The very small vestige of hydrogen cyanide thus set free can have no effect, and therefore I let you smell it. Slight traces are also found in bitter almonds; that accounts for the similarity of smell. Potassium cyanide easily dissolves in water and breaks up into potassium ion and cyanogen ion. I add a little silver nitrate to the diluted solution—

P. A precipitate is thrown down; it looks just like silver chloride.

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M. It is silver cyanide, AgCN. This shows you very clearly the resemblance between the compound cyanogen ion and the simple chlorine ion. We will now take leave of cyanogen and carbon for the time being; we shall often meet them again later on.

23. SILICON.

M. What were the more important topics of yesterday's lesson?

P. There were many. I learned how to calculate the heat effect of such reactions during which it cannot be measured directly; also, that there are chemical compounds which, during formation, absorb instead of give out heat. And I studied some of the organic groups, more especially the hydrocarbons. They form series in which the successive members differ by one carbon and two hydrogen.

M. And substances which vary in this way have very similar properties; in particular the boiling- and melting-points rise as the proportion of carbon increases.

P. Yes; and petroleum consists of hydrocarbons; so do vaseline and paraffin.

M. Good; that will do. To-day let us study a new element, silicon, which is widely distributed all over the world. You already know that flint is an oxide of this element. (I. p. 103.) Since it is difficult to remove the oxygen, silicon itself is not very easily prepared. Here are two samples.

P. They look quite different.

M. Silicon has several allotropic forms. This brown powder corresponds to amorphous charcoal and these grey, glittering crystals to graphite. However, we do not need to bother ourselves much with these varieties, since this element is of no manner of use and also has no properties of special theoretical interest. But we must give some attention to silicon dioxide, SiO_2.

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P. Is it the same as flint?

M. Flint is one variation of it. The purest form is *rock-crystal*, which is beautifully transparent, like glass, and rises to a point in hexagonal columns, resembling six-sided pyramids. It is often mixed with some foreign substance which imparts to it a violet, rose, or greyish-brown colour; and these varieties are known as *amethyst*, *rose quartz*, and *smoky quartz*. Ordinary quartz is rock-crystal to which some impurity has given a dirty white appearance.

P. How does this impurity get there?

M. The rock-crystal has probably been slowly deposited, during the course of many centuries, from water which contained silicon dioxide, or rather silicic acid, in solution. This water would dissolve other substances of all kinds, and these would contaminate the precipitate.

P. What makes us suppose that this extraneous substance gained access in this way?

M. Smoky quartz becomes colourless if we heat it, showing that its colour is destroyed by heat. Consequently it can never have been molten.

P. Perhaps the colouring matter got into it afterwards?

M. It is much too solid for that. Besides, we have found pieces of quartz the size of a man, and the interior was no clearer than the outside. That argues against your supposition.

P. You said something about silicic acid?

M. Yes; silicon dioxide is the anhydride of this acid; but unlike those of which you have hitherto heard, this anhydride neither dissolves nor forms an acid on coming in contact with water.

P. Then how do we obtain this acid?

M. From its salts. Of these many of the silicates of the metals occur in nature, especially those of potassium, sodium, calcium, aluminium, magnesium, and iron. They form a very large proportion of the earth's crust. Ordinary *granite*, for example, consists principally of quartz, which appears as

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whitish crystals; of felspar, which forms reddish crystals; and of mica. *Felspar* is a silicate of aluminium and potassium; *mica* is mostly composed of the magnesium and aluminium salt. Clay and slate are silicates of aluminium; and, with the exception of limestone and the minerals, there are few portions of the earth where salts of this acid are not to be found.

P. Then what is silicic acid itself like?

M. Your question is not easily answered. The pure acid is hardly known as an individual compound, and its solution in water has not the same properties, excepting that both are colourless. The best I can do is to show you its derivatives. This syrupy liquid is a watery solution of sodium silicate.

P. It looks quite different from the other salt solutions.

M. But it is not. If we melt quartz, or another form of silicon dioxide, with sodium carbonate, carbon dioxide is given off and sodium silicate is left behind. It looks just like glass, but differs by dissolving in boiling water. It is therefore called water-glass.

P. Then what is glass itself?

M. It is a mixture of sodium and calcium silicate. You see even here we find silicon. If I now decompose this sodium silicate solution with an acid, say hydrochloric acid, silicic acid separates out.

P. It looks like thick gelatine.

M. Yes. It has never been obtained as crystals, and in this it is exceptional. I now repeat the experiment, after diluting my solution with a considerable quantity of water.

P. Nothing happens.

M. On the contrary, silicic acid has been formed; but it does not precipitate.

P. Perhaps it is slightly soluble and dissolves in much water, but not in a little.

M. That is not the case; for if I add water to the silicic acid produced in my first experiment it does not dissolve.

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P. I do not understand this.

M. If I evaporate this solution, which has given no precipitate, and drive off the water, then the silicic acid separates out; and on adding water none of it will dissolve again.

P. So it will not go into solution after it has once been solid?

M. That's it. This behaviour is connected with the fact that silicic acid cannot crystallize. We call such substances colloids, from the Latin *colla*, meaning glue (for this also behaves in a similar manner). The colloids have very remarkable properties. We are only just beginning to investigate them.

P. I can see no particular resemblance between silicic acid and glue.

M. Let me show you one. I take a little dilute water-glass solution; add some litmus—

P. It turns blue immediately!

M. Yes. These salts are split up by water into acid and base, for silicic acid is an extremely weak acid. This is also the reason it has no action on litmus; but the liberated sodium hydrate has, and so it gives the blue colour.—I cautiously add hydrochloric acid until the blue just changes to red.

P. Nothing has separated out.

M. Wait a little. The solution, which was originally transparent, now begins to become cloudy; and now I can turn the glass upside down.

P. The silicic acid has become stiff, like gelatine. Yes; here it does indeed look like solid glue.

M. Whether it comes out of solution or not depends on several circumstances. The easiest way to obtain it in this form is to make the solution neutral; if either acidic or basic it is much more difficult to cause the separation.

P. Why is this?

M. We cannot yet say. Now since silicic acid is so weak it plays an important part in the changes which affect the

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earth's surface; for its salts become decomposed by the carbonic acid in the air.

P. But, still, this also is a very feeble acid.

M. Quite so; but nevertheless it acts on litmus, and silicic acid cannot; nor does the latter taste sour nor give off hydrogen with magnesium.

P. Then what right have we to call it an acid?

M. Because it forms salts. In fact, this is the most important thing about it. These salts, of which so many of our rocks and cliffs consist, are thus attacked and converted into other compounds by the carbon dioxide and vapour of the atmosphere; and we describe the disintegration which ensues as a *weathering* process.

P. But any effect must be inconceivably slow, for the mountains remain unchanged through centuries.

M. The result is, indeed, slow; but even mountains are altered by it in time. Streams are continually carrying away into the valleys the worn particles in the form of mud, sand, and stones.

P. Then that means that all the hills will one day be washed away!

M. Well, this transformation is not near, but only half way towards, completion. The rivulets leave the stones and carry the mud and sand into the rivers; these bring the mud and part of the sand into the sea where they sink to the bottom and become slowly moulded, with their history, into solid rock. There chemistry must leave them for the present. But to return to the silicic acid, some of it is dissolved and then, in process of time, separates out as silicon dioxide, partly in the form of quartz, partly as amorphous or non-crystalline varieties, such as *flint* and *opal.*

P. Let me go back a bit. I had no idea that the whole world was, so to speak, a chemical laboratory. Of course, I knew that the economy of plants and animals was regulated according to chemical laws; but I did not imagine

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that those dead stones were in continual chemical activity.

M. These processes are so slow that their effects are not easily noticeable; but the results are just the same whether the reaction is fast or slow.—We have now done with the non-metals, and we ought to pause here a little before commencing the study of the metals. In the meanwhile you can go over for yourself all that you have just learned.

24. THE METALS. SODIUM I.

M. To-day we enter on a new section of inorganic chemistry, the study of the metals.

P. You told me, at the beginning, that by far the greater number of the elements were metals. So it will be long before we finish them, judging from the time we had to devote to the fewer non-metals.

M. We shall not be long over them. We shall not give so much attention as hitherto to each separate element, because the general laws took up so much of our previous time and these we shall, in future, only need to apply and not explain. But besides this, the chemistry of the metals is, on the whole, much simpler than that of the non-metals.

P. Why is this?

M. The compounds of the metals are, in the great majority of cases, of the nature of salts. Now you know that the reactions of a salt, when dissolved in water, depend on the behaviour of its ions (p. 94). Many metals form just one kind, namely, the simple or elementary ion; others two, or, at the most, three kinds. Also, compound ions are much more prevalent with non-metals than with metals. Therefore, the chemical characteristics of the latter are proportionately simple.

P. That's a comfort.

M. I thought you were fond of learning chemistry?

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P. So I am. But I always get afraid when I hear about applications, or remarkable properties, and other strange scientific terms.

M. You ought to have no further difficulty on this account. For some of the metals, such as iron, copper, lead, are familiar to us as among the oldest and most important raw materials in the arts and manufactures. Besides, you will soon see that all their peculiarities are subject to universal laws, and you will recognize this as we go along. You will, later on, find a special pleasure in tracing the effect of these general rules in their application to individual substances.

P. I have often thought over this, and I find that the application is really the effect. The laws are only theoretical.

M. That is because you look on them in a so-called practical sense. But just consider: why did I tell you about these various laws?

P. It is difficult to answer that. Was it so that I might make use of them?

M. Yes; of course. By applying the correct laws you can prophesy what is going to happen.

P. Oh! But man cannot foretell the future!

M. Certainly he can. You yourself did so this very morning; for when you were on your way to school you knew beforehand that I would be there to teach you. Otherwise you would not have come.

P. Yes; if you put it that way. But there was just a chance that you might not have been here.

M. No; there was no chance; for I have undertaken this teaching as a duty which I would only omit if I were ill. So there was every probability that I would be here, and, therefore, you came.

P. But still probability is not certainty.

M. Certainty is nothing more than a very great probability. You consider it certain that the sun will rise to-morrow morning. That is a prophesy which you can make with certainty.

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P. There is nothing wonderful about a prediction of that kind. Everyone knows it.

M. Just so; it is a law of nature with which all are familiar. We can foretell, with equal surety, when a solar eclipse will take place. Everyone does not understand the laws of nature on which this prophesy is founded, but nevertheless we look upon its fulfilment as a certainty because all the astronomical forecasts which have hitherto been made by scientists have come true.

P. Simply because they were able to make the correct calculations.

M. Still, the fact that we here depend on certain numbers does not weaken the case, but rather the reverse. For if we know the conditions so intimately that we can use accurate measurements relating to them, then surely we can prophesy with absolute accuracy. The calculations are only means which ensure our predictions being fulfilled as exactly as possible.

P. But it has happened, in several instances, that what was foretold by theory has turned out quite otherwise in practice.

M. Then the theory was wrong, or, as happens more frequently, was wrongly applied. The best of theories is of no value to one who cannot adapt it to his use.

P. But when all is said practice is more convincing.

M. I do not understand you.

P. I mean we know about the conduct of a process with greater certainty after it has occurred than we could discover beforehand by simply foretelling.

M. In the first case we know what has happened under certain definite conditions; but if we wish to draw a conclusion as to what will happen in future cases we must, either tacitly or expressly, admit the existence of a law of nature in supposing that the process will repeat itself the next time in the same way as before.

P. But that follows as a matter of course.

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M. I have already often told you that we describe anything about which we have not thought as a matter of course. This is how the practical man regards a law of nature governing any phenomenon which, the conditions affecting it being always the same, is frequently repeated. But in order for our forecasts to be fulfilled we must know all these conditions, and science generally enables us to find out what particular influences we have to take into consideration. What we in ordinary life call practice is only a more accurate, empirical knowledge of a definite phenomenon and the circumstances which usually attend it, i.e., it is nothing more than a theory deduced from a circumscribed instance.

P. But still the practical man is generally more reliable than the theorist.

M. He is, inasmuch as he is more intimately acquainted with the narrow sphere bounded by his practical experience. But when new conditions, of which he is ignorant, arise he does not know what to do. He must then have recourse to science. Your ideas are those of an earlier, a less developed age. Indeed, the fact that the large chemical manufacturers have in their pay hundreds of scientific, i.e., theoretical chemists, is a proof that theory goes hand in hand with practice. And everywhere, in other branches of life, we are making more and more use of science. The great practical advances which the medical profession, for example, has made are due to theoretical research.—But we must return to our metals. We shall first take sodium. This you have already often seen. What do you know about it?

P. It is a light metal, white like silver, and combines very readily with oxygen, which it can therefore extract from all sorts of compounds. For example, it easily decomposes water in this way.

M. What is formed? Write the equation.

P. $Na+H_2O=NaOH+H$. Sodium hydroxide or caustic

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soda is produced, and at the same time hydrogen is given off.

M. You have already met with caustic soda. What do you know about it?

P. It is a white substance, easily soluble in water; the solution turns red litmus paper blue. It is a base.

M. What is that?

P. A base can form salts with acids. It is generally a compound of a metal with hydroxyl, i.e., one oxygen and one hydrogen. For instance, sodium hydrate acts with hydrochloric acid thus: $NaOH+HCl=NaCl+H_2O$. The hydroxyl of the base and the hydrogen of the acid unite to form water, and the remaining constituents produce the salt.

M. Right; and these "remaining constituents" of the acid and base we call ions. What kind of a salt is NaCl?

P. It is our ordinary white kitchen-salt.

M. Yes. Let us study it for a little. Sodium chloride is the most widely distributed of all the sodium compounds present in nature. It is found in enormous quantities dissolved in sea-water; and also, in the solid condition, as *rock-salt.*

P. I saw some rock-salt the other day, but it looked red.

M. Little scales of iron oxide are usually mixed with it; these cause the red colour. When pure, it crystallizes in perfectly water-clear, transparent cubes. It dissolves freely in water, as you know; 100 parts of water take up 36 parts at the ordinary temperature, and 39 parts at 100°. So its solubility hardly varies at all with the temperature. This is a singular property of sodium chloride which you will not find with other salts.

P. Yes; it is remarkable. I thought that all substances had to dissolve in larger quantities in the heat than in the cold, just as all liquids evaporate faster on warming.

M. The latter is certainly the case; and, indeed, evaporation and solution are similar in several ways; but

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this is not one. In fact, we shall later on meet with salts which are less soluble at a high than at a low temperature.—We prepare the other sodium compounds from rock-salt.

P. Why do we not use sea-water salt? It would be cheaper, as we have to dig the other out of the earth.

M. It is not cheaper; for there are 30 to 50 parts of water to 1 part of solid in sea-water, and the heat necessary for its evaporation requires more fuel than the salt is worth. But in very hot countries, where this work can be done by the sun, large quantities of salt are obtained by allowing sea-water to evaporate. However, we occasionally find on dry land natural salt springs which contain much more dissolved sodium chloride than sea-water does. These are made to yield their supply by first allowing the solution to evaporate as much as possible by slowly trickling down long and high walls of brushwood exposed to the air. These erections are called *graduators*, because the percentage of salt is graduated and is wont to be estimated according to its progress over them. The liquor is afterwards dried down in large pans over a fire.

P. Why do they not complete the evaporation by exposure to the air? It would be much cheaper.

M. This could only be done in a very dry atmosphere or hot sunshine, otherwise it would take too long and so prove costly. Ordinary salt is used, of course, with food; but far the larger proportion is used in chemical industries, chiefly for the preparation of caustic soda and soda crystals.

P. Then we have to remove its chlorine.

M. Quite right. Caustic soda is made by electrolysis (p. 66.) The ions of ordinary salt are the chlorine ion, Cl', and the sodium ion, $Na^{\cdot}$. The electric current causes the latter to travel with the positive stream, while the chlorine ion goes in the opposite direction and separates out at the anode, where the negative electricity leaves the solution. What is formed at the cathode?

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P. Sodium. You shake your head? Ah, I remember; the sodium decomposes the water and so does not appear as the element, but reacts and produces hydrogen and sodium hydrate. (P. 70.)

M. Right. That is how we obtain the caustic soda. In order that it may not unite with the chlorine at the anode we have to separate the two electrodes by a porous partition which can be penetrated by the current, but not by the liquid and gases. And since, unless they are of some resisting material, the electrodes are easily attacked by chlorine and sodium hydrate, we make the anode of platinum or artificial graphite; iron does for the cathode, since it is not effected by bases.

P. It must be a pretty complicated apparatus.

M. It is; and they are always making alterations in it, a sign that no practical method of working has yet been discovered.—Besides this electric decomposition, ordinary salt is made to undergo a chemical dissociation for the preparation of soda crystals.

P. I know these are white, but I am ignorant of their chemical composition.

M. *Soda crystals* or *washing-soda* is sodium carbonate. The formula is Na_2CO_3. In commerce we draw a distinction between crystalline and calcined sodium carbonate; the former contains water of crystallization, the latter is water-free. Calcined derives its name from lime (calcium oxide) burning, and means ignited until all volatile matters have been driven off. If we heat soda crystals they lose their water by evaporation.

P. I do not quite understand what "water of crystallization" means.

M. Many salts when crystallizing out from their solutions in water absorb water in doing so. Soda crystals, for example, have the composition $Na_2CO_3 + 10H_2O$. The elements of the water are chemically combined with the salt in proportions which are regulated by the law of combining weights, as

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expressed in the above formula. But on heating, water is given off as vapour and the water-free salt remains behind. Here you see the two varieties; both are white. Just calculate how much water the crystals contain.

P. Na_2CO_3 comes to 106.10, and $10H_2O$ to 180.20. Hulloa! They contain much more water than salt, and yet they are solid! Is the water present as ice? It looks like it.

M. Your calculation is correct, but not your conclusion. Remember what I said regarding a similar question sometime ago. We have no right to affirm that the crystals contain water as such, for then it must exert its properties and be a liquid. All we can say is that they part very easily with water, which again unites readily with the water-free salt and forms crystals.

P. But even you, yourself, speak of these substances as "containing water."

M. I have to retain this way of expressing myself because it is in universal use and you would not understand your other masters or lesson books were I not to accustom you to such phrases. But you must be on your guard against drawing wrong conclusions from them.—Now let us come back to sodium carbonate. You know that carbonic acid is a very weak, and hydrochloric acid is a very strong acid. (P. 88.) So we would not suppose it possible to prepare sodium carbonate from sodium chloride by driving out the hydrochloric acid with carbonic acid.

P. Then how do we manage it?

M. First of all by using sulphuric acid. You already know what this will form (p. 82). Write the equation again.

P. $2NaCl + H_2SO_4 = 2HCl + Na_2SO_4$.

M. Right. We can expel the hydrochloric acid by means of the strong and difficultly volatile sulphuric acid.

P. But then we are even worse off than before, for sulphuric acid will not beat a retreat before carbonic acid.

M. That is true; but let us try to remove it, not all at once,

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but bit by bit. The sodium sulphate is heated with carbon and the following reaction takes place:

$$Na_2SO_4 + 4C = Na_2S + 4CO.$$

Read the equation.

P. Sodium sulphate and carbon give sodium sulphide and carbon monoxide.

M. Sodium sulphide is the sodium salt of hydrogen sulphide, which has the formula—?

P. $-H_2S$. Yes; I see. Both the hydrogen are replaced by sodium.

M. Right. Then the sodium sulphide is decomposed by heating it with calcium carbonate, thus: $Na_2S + CaCO_3 = CaS + Na_2CO_3$. Read it!

P. Sodium sulphide and calcium carbonate give calcium sulphide and sodium carbonate. Yes, that gives us what we want.

M. Not quite. The two salts are still mixed together. But the carbonate is very easily soluble, while the sulphide is not. So we can separate them by extraction with water in the same way as we treated the sugar and sand. (I. p. 14.)

P. And finally we have to evaporate the water in order to obtain the soda crystals from the solution. The whole preparation must occupy some time.

M. It does not take so long after all, for we can decompose the sodium sulphate and carry on the calcium carbonate reaction at the same time. So we have the following stages: first, ordinary salt is treated with sulphuric acid, and we have hydrochloric acid as a by-product. Then the sodium sulphate is mixed and heated with carbon and limestone, when carbon monoxide is given off and the sodium sulphide reacts with the calcium carbonate. Lastly the two salts are separated by lixiviation, and the sodium carbonate is obtained by evaporation. We will learn another method of preparing this to-morrow.

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25. SODIUM II.

M. What did you do yesterday?

P. I learned how to make caustic soda and soda crystals. The preparation of the former was much the simpler. Can we not make the carbonate by electricity?

M. Certainly, all we require to do is to pass in carbon dioxide near the cathode during the preparation of the sodium hydrate, which then changes into the carbonate. Write the equation.

P. $NaOH + CO_2$—no, that won't do. I must take two sodium hydrate.

M. As it happens, you were about to write the correct equation. It should read: $NaOH + CO_2 = NaHCO_3$. We obtain, not the neutral, but the acid carbonate.

P. Ah; I understand. Carbonic acid is dibasic, and can therefore have two sodium salts; the neutral, Na_2CO_3, and the acid, $NaHCO_3$. Why is the latter formed in this case?

M. It is very much less soluble than the neutral salt, and so separates out from the solution, no evaporation being necessary. I have here a concentrated solution of soda crystals; I pass in some carbon dioxide from our old apparatus (I. p. 238); the following reaction takes place:

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3.$$

P. Why did you insert water?

M. Since carbon dioxide is an anhydride, water is necessary for the preparation of its acid.

P. A quantity of crystals has formed!

M. This new salt, the acid-sodium carbonate or sodium-hydrogen carbonate, is probably already known to you. It is also called sodium bicarbonate, because it contains twice as much carbonic acid as the neutral salt. It is taken as a remedy for simple stomachic troubles.

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P. Yes; I know it well. But why is so much of the crystalline soda made?

M. Because it is used for many purposes in industrial chemistry. It and sulphuric acid are to the chemical manufacturer what iron is to the engineer.

P. I realize that sulphuric acid should be so because it has strong acidic properties. But what use do they make of sodium carbonate?

M. It can be employed in many cases instead of caustic soda; for since carbonic acid is very weak it can be easily expelled and the carbon dioxide then escapes as a gas. Here is a solution of sodium carbonate. Just test it with red litmus.

P. It turns blue. How is that? The salt is surely neutral?

M. It is the same here as with the sodium silicate. The acid is not strong enough to prevent its salt from being split up, to some extent, by the water into acid and base, and the latter gives the basic reaction. Sodium hydrogen carbonate is, on the other hand, neutral to litmus, because the decomposing effect is arrested by the balance of acid. You see that the names neutral and acid have somewhat different meanings, according as they refer to the composition of a salt or the reaction of a solution.—But we have still to consider a number of other sodium compounds. You have already met with sodium sulphate in connection with sulphuric acid. (P. 148.)

P. Yes; it is Glauber salt, and is used in medicine.

M. I can make use of this substance in explaining to you an important question regarding solubility. Let us construct a curve diagram (Fig. 28) as before (I. p. 212); marking off the divisions of the thermometer along the horizontal base, and letting the vertical numbers represent the parts of salt dissolved in 100 parts of water. In order to show the solubility of ordinary kitchen-salt we find the two points on the diagram which denote that 36 parts are soluble at 20°

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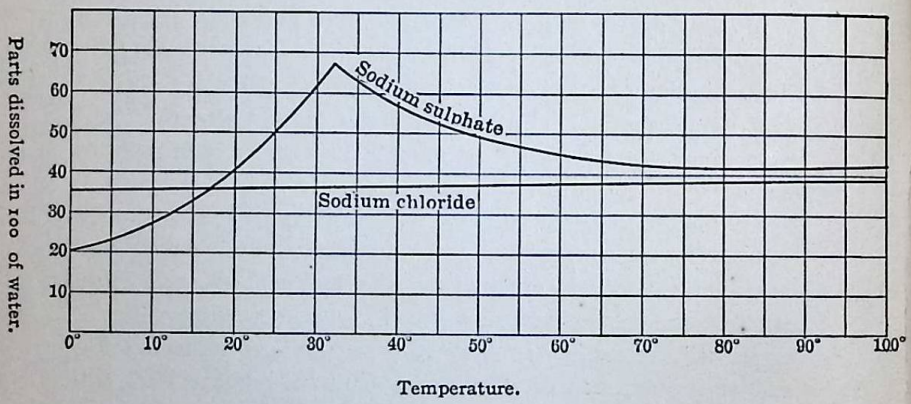
and 39 parts at 100°, join these with a straight line, and then any other point on this line shows the amount dissolved at any intermediate temperature.

P. Is that quite reliable? Might not some of the intervening ratios lie off this line?

M. Quite so. We have no right to be satisfied only with these two, if we know nothing more regarding the solubility of the salt. But we have defined several other points in addition to these, and it is permissible by the law of con-

FIG. 28.



tinuity (I. p. 200) to unite them by a continuous line, which is found to be very nearly straight. But now look at the other, the sodium sulphate curve. Tell me what you make of it?

P. At first, i.e., at the lower temperature, the solubility increases rapidly; then it passes onto a different curve and diminishes as the temperature rises.

M. Very good. You have interpreted correctly. But you must also notice that the law of continuity apparently lapses at 32°.

P. I thought as much, but did not dare to say so.

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M. That was a pity; for I would have been pleased to hear your opinion.

P. Well, I thought you would rather not, as you had only just been speaking of this law.

M. And you did not wish to make me feel embarrassed? That was a superfluous precaution, for I am not answerable for the laws of nature; and if they were irregular in any particular I would, far from remaining silent, take all the more care to tell you so as to prevent you from applying them falsely.

P. I see my mistake. But what happens to the continuity in this case?

M. Let me first show you another experiment. I have some Glauber salt here in this flask. I warm it gradually over the water-bath, and stir with a thermometer.

P. It is melting. The thermometer stands at 32°.

M. Yes; and if I now continue to heat the temperature remains steady, as it does while ice melts. Just look again.

P. The mercury is still at the same point. But now it appears to be rising; yes, it mounts higher and higher, and yet all the salt has not melted. Surely this, again, is contrary to a law of nature.

M. Aha; you have plucked up courage. The contradiction is only apparent; for the solid substance which you see in the flask is no longer Glauber salt.

P. What can it be then?

M. It is water-free sodium sulphate. At 32° Glauber salt which, like sodium carbonate, crystallizes with $10H_2O$, decomposes and forms a saturated solution of the water-free salt, some of which separates out. Therefore, we have to do with a more complicated process than actual melting. So long as any undecomposed crystals, $Na_2SO_4 + 10H_2O$, are left the temperature remains unchanged, as you noticed at the beginning.

P. I understand. But what has this to do with the peculiar solubility curve?

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M. It provides an explanation. Glauber salt containing water of crystallization can only exist up to 32°; it decomposes at a higher temperature and is then present as the water-free compound. Therefore, the first, the ascending portion of the curve, refers to the Glauber crystals; the second, the descending portion, to the water-free sodium sulphate. So there are two different lines, and consequently we cannot apply the law of continuity to both taken together.

P. I do not quite understand; for in both cases we have the very same thing in the solution.

M. Yes; certainly in the solution, but not dissolved. In the first place we have a solution of the crystals; in the second of the water-free salt. At the point of saturation the solid and the solvent are in equilibrium; so both must be taken into account; and if one changes the other must also.

P. Ah; now I understand. I would never have found cut by myself.

M. I don't think you would. It was a good long time before we were able to explain it. Glauber salt is not the only substance which has this peculiarity. Very many salts crystallize in different forms, containing different proportions of water. Each variety has its own series of saturation points; so a salt has as many solubility curves as it has different forms; and these curves intersect at the temperature at which one form changes into another. Sodium carbonate, for example, behaves very similarly to Glauber salt; so does sodium phosphate.

P. I have never seen this last substance.

M. Here is some. It does not look very different from the carbonate, for most of these crystals are coated with a white powder which is due to decomposition.

P. What causes this?

M. Salts containing water of crystallization part very easily with water; it even evaporates on exposure to the air;

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then a fine powdery substance is left behind containing little or no water. This process is called efflorescence. Ordinary sodium phosphate is the second salt of phosphoric acid which, you know, is tribasic. Do you remember its formula?

P. Yes; H_3PO_4.

M. Right. Only two of the three hydrogen are, in this case, replaced by sodium, so the formula is Na_2HPO_4. It is associated with 12 molecules of water of crystallization, and is the familiar phosphate of the laboratory where it is of great use in analysis.—I will now show you another interesting salt, sodium thiosulphate.* It forms large, colourless crystals. You have not yet met with its anion.

P. Has it not something to do with photography?

M. Yes. Photographers often have occasion to use it, as it dissolves all the salts of silver, and these enter largely into their processes. Its composition is $Na_2S_2O_3+5H_2O$, so its anion is S_2O_3''; and if you compare this formula with that of the sulphate ion, SO_4'', you will see that they are similar. The thiosulphate ion is simply the sulphate ion with one oxygen replaced by one sulphur. This is expressed by its name, for *thion* is the Greek for sulphur. It is obtained by heating sodium sulphite, Na_2SO_3, with sulphur:

$$Na_2SO_3+S=Na_2S_2O_3;$$

in the same way as sodium sulphate is prepared from the sulphite by adding oxygen:

$$Na_2SO_3+O=Na_2SO_4.$$

If we warm the crystals, they melt at 56° to a clear liquid. So, in this respect, they differ from Glauber salt. (P. 213.)

P. Yes. Why does nothing separate out?

M. Because the water of crystallization is sufficient to dissolve the water-free salt.

* This is sold and known to photographers as "hypo" or hyposulphite of soda, a name that is chemically incorrect.—TRANSLATOR.

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P. So it depends on this whether crystals containing water will melt completely or not?

M. Quite right. The thiosulphate is now quite melted; I let it cool. If we close the mouth of the flask with a plug of wadding the liquid will cool to the ordinary temperature and lower without solidifying.

P. This is an instance of supercooling?

M. Yes. I am fusing a little of the thiosulphate onto this glass rod in order to show you an important effect. I have another flask here containing liquid thiosulphate; I melted it yesterday, so it is quite cold. I dip in my glass rod—

P. Oh! How beautiful! You can see the crystals forming!

M. I draw it out again; the whole cluster of crystals clings to it, and now the formation of crystals does not continue in the liquid. This shows you that the crystallization is the result of a reciprocal action between the solid substance and the liquid. A supercooled solution is not unstable of itself; it only becomes so when we introduce the appropriate solid. Crystallization then ensues over the surface of mutual contact; but as soon as the cause is removed the solidification ceases.

P. I would like to repeat this experiment myself. May I?

M. Certainly. There is plenty of thiosulphate for you; it is very cheap. Only you must be careful, for the smallest speck of solid salt causes solidification. However, you can always remelt it and try over again; just add a little water to replace what has evaporated.—Well, these are the most important things I had to say about sodium.

P. But I have not yet discovered how to prepare sodium itself.

M. We obtain it by electrolyzing a melted salt. The most convenient one to take is sodium hydroxide, because it melts easiest. Sodium is now prepared in large quantities for use in chemical industries.

P. But how do they keep it? Do they store it, under petroleum, in large casks?

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M. They make it into square ingots and pack them tightly into tin cases, which are then hermetically soldered. In conclusion, I will show you how we can recognize sodium. I have here a platinum wire fastened into a glass tube—

P. How did you manage that?

M. You first heat the end of the tube so that the sides fall together; remove it from the flame and stick the end of the platinum through the orifice before it closes. Then continue to heat until the glass is neatly fused together and holds the wire firmly. (Fig. 29.) If I take up a trace of a

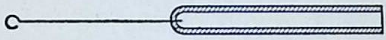

FIG. 29.

sodium salt on the small loop at the end of the platinum and ignite it at the burner it immediately imparts a brilliant yellow colour to the flame. This is caused by the sodium and is a means of discovering its presence since no other element produces this effect. (I. p. 145.) A flame is usually yellow, because sodium is to be found everywhere. Here is another platinum wire, which has been cleaned by being heated red-hot; it gives no colour to the flame. But if I merely draw it through my damp fingers it makes the flame yellow—

P. Yes; so I see. But just for a little.

M. That is a good way of distinguishing between the traces of sodium scattered round about and any somewhat larger quantities. The greater the amount present the longer and the brighter will the flame burn yellow.—I wish you to notice that all the sodium salt solutions which you have seen are colourless. And so it follows that the sodium ion, which was present in all of them, is likewise colourless. I cannot give you any other test for sodium; but the yellow

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flame effect is so delicate and characteristic that no other is necessary.

26. POTASSIUM AND AMMONIUM.

M. To-day we will not go over what you learned last time; for in discussing these other two substances we shall so often have occasion to refer to similar instances in yesterday's lesson that this will serve the same purpose as a repetition. You already know something of potassium?

P. Yes; it is a light metal, very similar to sodium.

M. Here is a specimen. It is really exactly like sodium, namely, silver-white; but we can only see the colour on a freshly cut piece, for it oxidizes very quickly in the air. It likewise decomposes water. I throw a small piece into a dish of water—

P. How it burns! What a pretty red flame!

M. The reaction is so vigorous that the hydrogen given off catches fire at once. The red colour is due to the potassium vapour, which burns violet-red, just as sodium gives a yellow flame. Test the water with red litmus paper.

P. It turns blue. Then a base has been formed? Let me write the equation: $K+H_2O=KOH+H$.

M. Right. You see how similar the two metals are. I have already shown you potassium hydrate or caustic potash, and you saw that it appeared and behaved the same as caustic soda. Their methods of preparation are similar, caustic potash being produced by the electrolysis of potassium chloride.

P. Then is the latter found in nature like ordinary salt is?

M. Yes; but not so abundantly. However, they sometimes come on a supply of potassium chloride, KCl, in the vicinity of deposits of rock-salt, to which it then bears a strong resemblance, being in the form of transparent crystalline cubes. It

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is known to mineralogists as *sylvine*. It is very much scarcer than rock-salt.

P. Is it present in sea-water?

M. Only in small quantities. But in many parts of central Germany they find deposits of another salt which consists of potassium chloride and magnesium chloride. It is called *carnallite*, and is the source of the potassium chloride used in industrial chemistry and in agriculture.

P. In agriculture?

M. Yes. Compounds of potassium are necessary for the building up of the framework of plants. If these cannot obtain sufficient from the soil we must give them some or they will become stunted. We supply it in the form of the potassium chloride obtained from carnallite.

P. Plants seem to require all sorts of things. First nitrogen, then phosphoric acid, and now potassium.

M. And above all, radiant energy. However, these supply all their wants; for whatever else they need, carbon dioxide, water, lime, iron, etc., is to be found nearly everywhere, in abundance, in the air and the soil. But these three elements, nitrogen, phosphorus, and potassium, are present in quantities insufficient for the demand; and, therefore, we have to supplement them if we wish to take full advantage of the sun's energy.

P. Could we not give them sodium, say as ordinary salt?

M. That is of no use; because, in this respect, the two elements are dissimilar.

P. What is the reason?

M. Probably this. If we treat arable land with potassium salts they are retained and we cannot wash them completely away with water. Sodium salts, on the contrary, are easily carried off. Therefore, plants are much more likely to meet with the former in the soil, for should any sodium compound find its way there it would be quickly swept away by the rain. Such plants as can assimilate and have an affinity for potas-

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sium thus have much more prospect of surviving, and so possibly they alone are able to attain maturity and propagate.

P. Hm; I understand.

M. That explains why certain kinds of vegetation, which flourish at the sea-coast or on the salt-fields, contain sodium instead of potassium. It is only in places like these, where sodium is plentiful, that "sodium plants" can exist. By burning vegetable organisms we can extract from their ash the metallic carbonates; namely, soda crystals from those grown by the sea, and pot-ashes from those reared inland.

P. What a curious name *pot-ashes* is.

M. It is the old name for potassium carbonate, K_2CO_3. I have just told you that they obtained it by lixiviating the ash with water. Well, the solid was then obtained by evaporation in pots. When purified it forms a confused mass of white crystals. It is very soluble in water.

P. Do they make it in this way now?

M. No. Since we have given up burning wood we no longer have any wood-ash to dispose of. It is now prepared from potassium chloride in the same manner as sodium carbonate is from sodium chloride, only on a much smaller scale, for there is little demand for it. It behaves just like sodium carbonate; its solution in water is basic to litmus, and gives a precipitate with carbon dioxide since the acid carbonate, thus produced, is difficultly soluble. Write the equation.

P. $K_2CO_3 + CO_2 + H_2O = 2KHCO_3$.
This is the same as the sodium reaction.

M. Yes; you may use potassium carbonate to repeat our former experiment for yourself. Here is the salt.

P. It is quite damp.

M. Because it absorbs water from the air and eventually deliquesces into a concentrated solution. It is, therefore, a desiccator, like sulphuric acid (p. 79).—You have already seen some of the other potassium salts, such as saltpetre

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and potassium chlorate. What do you know of the former?

P. Saltpetre is potassium nitrate, KNO_3, and is formed when nitrogenous substances decompose in the air. The potassium comes from their ash.

M. What does saltpetre look like?

P. It is a white salt, which dissolves in water.

M. Right. It is not very soluble in the cold; but becomes much more so if the temperature is raised. 100 parts of water dissolve only 13 parts at 0°, and 247 parts at 100°. It is used in the preparation of gun-powder because of its oxygen, which burns up the carbon and sulphur mixed with it. The following pretty experiment will show you this effect: I heat some potassium nitrate as strongly as I can in a small flask. It melts fairly easily to a colourless liquid; then bubbles are given off; these are principally oxygen. Now I throw in a small piece of sulphur—

P. It sparkles just as phosphorus does when burning in oxygen.

M. Yes; the temperature is very high, because the saltpetre is hot to begin with, and there is now the additional heat produced by the combustion of the sulphur.—Potassium chlorate parts with its oxygen much more easily.

P. Yes; we made use of this property to prepare oxygen.

M. For that reason, potassium chlorate is rather a dangerous substance. When it was discovered a hundred years ago they tried to make gun-powder from it, but the whole powder-mill was blown into the air and several men were killed. I mix some with this black powder, which is called antimony sulphide, and take good care not to prepare more than the size of a peppercorn. I have to do the mixing with a feather, for an explosion would ensue were I to use a pestle and mortar. I wrap the mixture in paper, lay it on an anvil, and strike with a hammer—

P. Bang! Just like a gun.

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M. You already know the other characteristics of potassium chlorate (p. 104).—Here are still other salts of potassium for you. This is the bromide, KBr, and that is the iodide, KI. Both form water-free crystals. You can take special note that this is the condition of all potassium salts, while nearly all sodium crystals contain water.

P. You did not tell me that kitchen-salt contained water.

M. Ordinary kitchen-salt does not. But if we allow it to crystallize from its solution at a temperature somewhat below 0° the crystals take quite a different shape and are combined with $2H_2O$. But they decompose even at $-2°$ into the water-free salt and its saturated solution, just as Glauber salt does at $+32°$. (P. 214.) The iodide and bromide of potassium are always water-free. It is as the latter compound that the bromine ion is brought on the market and put into use.

P. Please explain. Surely we cannot have the bromine ion by itself?

M. It is just because we cannot have an anion by itself that we have to take some cathion with it, so we choose the one which is cheapest and will give a salt with suitable properties. Therefore, if we have to employ bromine for any purpose we just take potassium bromide. Instead of potassium we could have sodium, or calcium, or any other metal. But calcium bromide is an extremely deliquescent salt, difficult to prepare and inconvenient to keep; therefore, it is not used, although calcium is much cheaper than potassium.

P. But so is sodium, I think. Why do we not take sodium bromide?

M. Principally from force of habit. We knew and got accustomed to the potassium compound before the sodium salt was discovered. Besides there is not a great difference in price, since the bromine is the chief factor in the cost.—Exactly the same thing applies to potassium iodide.

P. This salt has a yellow appearance.

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M. Pure iodide of potassium is colourless. But after a time the action of the atmospheric carbonic acid produces a trace of hydriodic acid, and this is decomposed by the oxygen of the air into water and iodine. (P. 130.) The latter causes the yellow colour. The salt is very soluble in water; and the solution, in its turn, dissolves large quantities of iodine, turning brown in the process.

P. And yet iodine is very slightly soluble in water. (P. 123.)

M. Yes; but when brought in contact with the iodine ion it forms a new ion with the composition I_3. This gives the brown colour to the solution, which can generally be made to serve the same purpose as free iodine, for the I_3 ion easily decomposes into the latter and the ordinary iodine ion. In other words the reaction, $I' + I_2 = I_3'$, goes as readily forward as backward.—Lastly, let me show you one other salt which is similar to potassium iodide, but differs in being very poisonous. This is potassium cyanide, KCN, the potassium salt of prussic acid. If you smell it cautiously you can detect the presence of hydrocyanic acid.

P. I know the smell; it reminds me of bitter almonds.

M. Large quantities of this substance are used to extract gold from auriferous deposits, since the metal dissolves in a solution of the cyanide in water. However, they are beginning to take sodium cyanide instead, as it is somewhat cheaper and also contains more cyanogen.

P. How can that be; each salt contains one cyanogen to one metal?

M. That is so; but both compounds vary in gross amount. Just calculate for me the two combining weights.

P. KCN equals 65.19, and NaCN equals 49.09; both contain $14.04 + 12.00 = 26.04$ of cyanogen. Yes; now I understand; since sodium weighs less than potassium, sodium cyanide contains an equal amount of cyanogen in a less weight of salt.

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M. Right. Now a few words about the potassium ion. It is colourless—

P. Because all solutions of potassium salts are colourless.

M. Consequently they contain no coloured ions.

P. But are there ever any?

M. Certainly. You have already met with the greenish-blue copper ion, and you will soon come across several more which form compounds with potassium of a colour the same as their own.

P. Then does the tint of a salt solution depend on the colour of the cathions and anions?

M. To be sure; in the same way that all its other properties depend on these constituents.—We have a test for the potassium ion. It is the sodium salt of an acid containing platinum; the formula is Na_2PtCl_6. It is generally called sodium platinochloride and gives a yellowish-red solution. If I add some to a salt of potassium, a yellow, very difficultly soluble precipitate of potassium platinochloride is formed, especially if a little spirits of wine is present.

P. There is the precipitate. Its formula must be K_2PtCl_6?

M. Right.—Now we have to consider the ammonium salts.

P. These are derivatives of ammonia?

M. Yes. Ammonia unites directly with acids, and their hydrogen converts ammonia, NH_3, into ammonium, NH_4. The ion, NH_4, behaves so similarly to the potassium ion that the two are most conveniently studied in conjunction.

P. Is the former also colourless?

M. Certainly; it must be; since a solution of ammonia, which contains the ammonium ion, has no colour. The similarity to potassium is apparent in the degree of solubility and form of crystallization of their corresponding compounds. Let us begin with ammonium chloride. This salt differs from the others on account of its peculiar tenacity.

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You will notice this if you try to pulverize some. It is generally known as sal ammoniac.

P. How did it get that name?

M. It is a contraction for sal ammoniacum, salts of ammonia. It is used in soldering, because it decomposes into ammonia and hydrochloric acid on heating. The former escapes and the acid dissolves the skin of oxide which covers the surface of the metal. This is then able to adhere to, and be bound by, the liquid solder.

P. What sort of a substance is solder?

M. For soft solder we use an amalgam of zinc and lead, which melts easily.—I heat a little sal ammoniac in a test-tube—

P. A white substance deposits on the upper part; the intervening space is clear glass. At the bottom the salt remains solid, but is continually getting less and less. That is very remarkable!

M. You here see an instance of *sublimation*, i.e., evaporation without melting. The solid ammonium chloride has passed directly into a gas, and this has changed back again into the solid condition. I have already told you that the vapour is not ammonium chloride, but a mixture of hydrochloric acid and ammonia.

P. How did they discover that?

M. Well; it was not easy. They first estimated the density or molecular weight of the gas, and found it did not come to 53·53, as the formula, NH_4Cl, would have led us to suppose, but to just a little over half that figure. In order to explain this they assumed that the vapour was a mixture of ammonia and hydrogen chloride. The volume is then doubled and the density is half as great.

P. Hm; the actual result was hardly sufficient to justify this theory.

M. So many people thought, and therefore they had recourse to other evidence. This was forthcoming when they

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examined the vapour more closely. You remember that hydrogen disperses easily on account of its rarety (I. p. 137). It is a universal rule that the lighter the gas the more quickly does it dispose itself over a given area. Now the molecular weight of ammonia, 17.07, is less than half that of hydrogen chloride, 36.46. If sal ammoniac vapour is left exposed to the air for any time the lighter ammonia escapes and the hydrochloric acid remains behind. This separation can be easily indicated.

P. Can you show me how?

M. I would rather leave that till later on, as the experiment is not easily arranged because of the high temperature necessary for the volatilization of sal ammoniac. To show you the similarity between the potassium and ammonium ions: here is our sodium platinochloride solution, I add some to a solution of ammonium chloride—

P. There is a yellow precipitate, very like that produced by potassium.

M. But it is not quite the same. I add some potassium hydrate to the sal ammoniac solution, and warm in a test-tube. Just try the smell, and then see if you can explain it.

P. Ugh! It is ammonia. The equation is

$$NH_4Cl + KOH = KCl + NH_4OH.$$

But it is ammonium hydroxide, not ammonia, which is formed.

M. Just think. In what relation do these two stand to one another? Have you ever seen the hydroxide?

P. Ah! Now I remember: Ammonia is the anhydride of the hydroxide, and the latter decomposes into ammonia and water.

M. Very good; that is quite correct. But we need not use the nose for this test. A damp piece of red litmus paper serves the same purpose. Look here, it turns blue.

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P. So this would be a way to distinguish between ammonium and potassium salts?

M. Yes; analysts have adopted this method.—Now I must tell you of another important application of ammonia, its use in the preparation of sodium carbonate from ordinary salt. This is a much simpler process than the old one. (P. 208.) We decompose a solution of the salt with ammonium carbonate and pass in carbon dioxide. The following reaction takes place:

$$2NaCl + (NH_4)_2CO_3 + CO_2 + H_2O = 2NaHCO_3 + 2NH_4Cl.$$

Read it!

P. Sodium chloride, ammonium carbonate, carbon dioxide, and water give sodium bicarbonate and ammonium chloride. How is the weak ammonia able to remove the chlorine from the sodium?

M. This is an instance where the usual conceptions regarding the strength and weakness of acids would lead you into error; because here we have to deal not with acids, but with salts. In their case, it is a rule that, given a sufficiently concentrated solution, the least soluble combination separates out before any of the others possible.

P. What do you mean by "any of the others possible?"

M. Each salt consists of a cathion and an anion. If we have two different compounds with the cathions K′ and K″, and the anions A′ and A″, then four combinations are possible. What are they?

P. Now I understand. K′A′; K′A″; K″A′; and K″A″. Is that correct?

M. Yes. Well, look at the above equation, which represents the commercial process of manufacture, and let us suppose that ammonium bicarbonate is first formed. It has the ions $NH_4^{\cdot}$ and HCO_3', while those of the ordinary salt in the solution are $Na^{\cdot}$ and Cl'. These two compounds

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would react, and what would be the other combinations possible?

P. $NaHCO_3$ and NH_4Cl. Ah! These are what we already have. The equation would be:

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl.$$

M. Quite right. We now have to convert the valuable ammonia into the carbonate, so that it can be used over again; and we must also change the bicarbonate of sodium into the neutral salt. We obtain our first object by heating the ammonium chloride with calcium carbonate; ammonium carbonate then distills over and calcium chloride remains behind. On heating the sodium bicarbonate it splits up into sodium carbonate, water, and carbon dioxide:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2;$$

and the latter is collected for repeated use.

P. I can follow your reasoning, but I have not yet a thorough grasp of the whole question.

M. Actually this represents the whole process:

$$2NaCl + CaCO_3 = Na_2CO_3 + CaCl_2;$$

for the first two compounds arrive at the manufactory and the last two leave it. The ammonium salts only play an intermediate part as they are always used over and over again in the reaction.

P. Then why can we not simply leave them out?

M. Because the above equation will not go as I have written it; on the contrary, the reverse action takes place. I pour some sodium carbonate solution into a solution of calcium chloride; a thick, white precipitate of calcium car-

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bonate is immediately formed, while sodium chloride remains dissolved.

P. Because, in this case, calcium carbonate is the least soluble salt.

M. Very good. I see you can apply my teaching. But by the co-operation of ammonia we are able to obtain the sodium bicarbonate, since it is the most insoluble salt in that reaction; and it was because ammonium carbonate is more volatile than ammonium chloride that we were enabled to convert the latter into the former. For on applying heat the small amount of ammonium carbonate which is formed escapes, and therefore a fresh supply can be produced; this also is driven off, and so on, until the conversion is complete.

P. This is similar to what happens during the preparation of hydrochloric acid. (P. 82.)

M. Yes.

P. I am still not very clear about this matter; but I hope I shall feel more certain after thinking it over once or twice.

27. CALCIUM I.

M. You remember how I compared the study of chemistry to a walk along the paths of a forest?

P. Yes; and you were right. It is really very good fun learning chemistry.

M. I have reminded you of this because, as we proceed, we shall cross more and more of the paths over which we have already travelled. The element which will engage our attention to-day has already been long familiar to you in its compounds.

P. Yes; I know calcium carbonate; it is ordinary chalk. We make carbon dioxide from it. I also prepared a number of salts from calcium hydroxide, but I did not see them as they were all in solution.

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M. Well, let us start on them at once. Calcium carbonate can be obtained in several other varieties. Ordinary limestone, of which many mountains are formed, is one, this beautiful crystal is another. It gives a remarkable optical effect. Just lay it on your page and try to read through it.

P. How curious! The letters are all double.

M. This mineral is called *calcite.* It transmits light in such a manner that two images, instead of one, are formed in the eye.

P. What causes this, or rather, what is the explanation?

M. The shape of the crystal. You see it has oblique angles. Such a "double refraction" is shown by all crystals which do not form cubes, but the effect is seldom so clearly brought out as with calcite. Less transparent crystals of calcium carbonate are called *calcspar,* and when small and closely interlaced they are known as *marble.*

P. But marble is of various colours.

M. Only if foreign substances have been deposited amongst it during formation. When quite pure it is as white as loaf sugar, and almost transparent. How would you recognize if all these varieties were calcium carbonate? Think of the first time you met with this salt.

P. I would see if they effervesced and gave off carbon dioxide with hydrochloric acid.

M. Good. You would in that way prove them to be carbonates. And how would you tell them from potassium, or sodium carbonate?

P. Oh; both the latter dissolve in water, calcium carbonate does not.

M. Right. That would do, as far as it goes. We can prepare many of the other calcium compounds from limestone.

P. Yes; carbonic acid is so weak that it can be expelled by all the other acids.

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M. It can even be driven away without their aid. On applying strong heat the following reaction takes place:

$$CaCO_3 = CaO + CO_2.$$

Read the equation.

P. Calcium carbonate gives—calcium oxide—is that right? —Yes; and carbon dioxide. I have not yet seen calcium oxide.

M. Here is some. It looks just like the limestone from which we prepare it, because no melting but a simple shrinkage takes place during the transformation. Just calculate how much calcium oxide, or *lime*, the carbonate will yield.

P. $CaCO_3$ equals $40.1 + 12.00 + 48.00 = 100.1$; and CaO equals $40.1 + 16.00 = 56.1$. That is only a little more than half.

M. Good. Now let us dissolve or *slake* our lime. Just watch. I boil some water in a large basin and add some pieces of calcium oxide. What do you see?

P. Nothing at first. Now a hissing and boiling commences, although you have removed the burner, and even after adding cold water some reaction continues. The lime swells and expands considerably; now everything has changed into a white powder, which appears quite dry, although a large quantity of water must be there. Has it all evaporated? But, if so, where has the necessary heat come from?

M. There has been a chemical reaction:

$$CaO + H_2O = Ca(OH)_2.$$

Read it!

P. Calcium oxide and water give—yes, now I remember—calcium hydroxide.

M. Quite right. Calcium oxide is the anhydride of calcium hydroxide and combines with water with a great evolution of heat, just as sulphur trioxide did. (P. 145.) Now

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try if you can prove this to be the hydroxide by its properties.

P. It ought to dissolve easily in hydrochloric acid, but very slightly in water. May I see if it does? Yes; that is all right.

M. Do not omit the litmus test.

P. It should be basic and turn red litmus blue.—It does.

M. Calcium hydroxide is, and has been for long, prepared in this manner, by first burning limestone and then slaking the lime. It is also some times spoken of as lime for short; it is distinguished, when necessary, as *slaked lime*, the oxide being called *burnt lime*. The former has been employed since ancient times as a constituent of building-mortar. Have you ever seen this made?

P. Yes. The lime is mixed with sand and water, and then the mixture is laid between the stones or spread over the wall. It slowly hardens there, just like glue or paste, because the water evaporates.

M. What you said last, i.e., your explanation of the binding effect, is not correct. If you were simply to remove the water no fixing process would result. What really happens is that carbon dioxide is absorbed from the air and calcium carbonate is produced. This forms in crystals which cling together and make a solid mass, like limestone or marble. Just take a little old mortar from a wall and drop some hydrochloric acid on it—

P. It effervesces. Yes; there is carbonic acid there. But what purpose does the sand serve?

M. It only plays a mechanical part. Since the calcium carbonate produced occupies less space than the hydroxide which it replaces, flaws and gaps would be left as a result of the transformation. These disturbances are lessened considerably if we provide some other substance to fill up the interstices. Write the equation for the action of carbon dioxide on calcium hydroxide.

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P. $Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$. I see water is formed.

M. That explains why the walls of new houses, which had been thoroughly dried, become damp again and "sweat" when they are inhabited. The human breath contains carbon dioxide, and this reacts with the slaked lime. How could we prevent this inconvenience?

P. By passing carbon dioxide into the rooms.

M. Quite right. How would we set about it?

P. We could make some from limestone and hydrochloric acid.

M. A more practical plan would be to place large iron crates of glowing charcoal or coke in each chamber; these would give off the gas, and at the same time the warmth necessary to dry the moisture produced.

P. I have seen fires such as these in newly built houses, but I thought they were only to provide heat.

M. This shows you how easy it is to adopt erroneous scientific ideas. If we have followed a train of reasoning which seems to prove conclusive then we generally assume that the matter ends there. But accuracy is not always ensured by, and may have little to do with, the justification of our theories.—However, let us return to calcium hydroxide. You already know that it is only very sparingly soluble: about 1 part in 500 parts of water.

P. Yes; the solution is called *lime-water* and can be used to test carbon dioxide.

M. Right. The solubility lessens as the temperature rises. In this calcium hydroxide resembles water-free sodium sulphate. (P. 212.) If you bring some clear lime-water to the boil it becomes distinctly cloudy. Of course, there is only a slight precipitate as the total amount dissolved is small.

P. You have not said anything about calcium itself.

M. Until a short time ago we knew almost nothing at all about this metal; but we recently learned how to prepare

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any amount by electrolysis. It looks like iron; is fairly hard; oxidizes in damp air to the hydrate; causes water to give off hydrogen; but is much less ready to form compounds than sodium, or even potassium.

P. And what of the calcium ion?

M. You remember, it was present in some of those salt solutions you prepared. (P. 22.) It is colourless and, as you must take special note, divalent. So far we have dealt with the alkali metals, which are monovalent, as is the ammonium ion also. The cathions of all the metals of the alkaline earths are divalent. Let us now turn to some of the salts of calcium, more especially to the sulphate. It is a substance well known as *gypsum*. Have you seen it?

P. I have seen statuettes made of this. They are of a white material, like chalk.

M. Crystalline gypsum is found in nature. It is sometimes in large, oblique-angled sheets, transparent as glass; at other times, it takes a striated form, like a mass of thin, closely packed threads, which have a silky sheen; and, lastly, there is granular gypsum. This is called *alabaster*. It is either white, or coloured by extraneous matter; is transparent; and is used for statuary and to make small articles of vertu. Here you see before you different specimens of natural gypsum. This mineral is extraordinarily flexible; the crystals stand a considerable amount of bending without breaking.

P. But none of these samples seems by any means so opaque as the small gypsum figures. Are they of the same substance?

M. The difference is merely mechanical. For the crystals found in nature are not simply calcium sulphate, $CaSO_4$, but also contain two molecules of water of hydration. By moderate heating we drive away about three quarters of this water and thus obtain burnt gypsum. If this is treated with water the mixture solidifies, after about a quarter of an hour,

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into a fairly hard mass which, on drying, becomes quite firm. It is this property that makes gypsum so useful.

P. What actually happens during this process?

M. The calcium sulphate again absorbs the expelled water of crystallization which is thereby changed into a solid form, and the crystals thus produced lace themselves together into a compact body. Since the pasty mixture is able to penetrate even into delicate moulds and "set" or solidify at the ordinary temperature, we can make it assume any shape we like.

P. Please show me this.

M. Let us take the cast of a coin. It must be cleaned and then given a rub with an oily rag so that the solid gypsum can be the more easily detached. I make a ring of paper round the coin, using sealing-wax to keep all firm; mix some gypsum with water to a fairly liquid consistency and pour it over the coin. After some hours you can disengage the hollow mould. If you let it dry and then rub it with a little oil you can pour some more of the paste into it and thus obtain an exact impression of the coin.

P. But how do they make the rounded statuettes?

M. The mould has to be manufactured in pieces, so designed that each can be removed without injury. These divisions are then joined together and filled with the gypsum paste.—However, all this has very little to do with chemistry. I will only add that calcium sulphate is soluble in water, though only slightly, 1 part in 400 parts of water; therefore, it cannot be employed as mortar for walls exposed to rain; on the other hand, it is often used for the interiors of buildings. Many natural springs contain small quantities of gypsum.—What do you know of calcium phosphate?

P. It is a constituent of bone, and is also found in nature. It is used as manure. (P. 178.)

M. Right. Just give me its formula.

P. Hm; I do not know if I can manage that. Phosphoric

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acid has three hydrogen and calcium is divalent. Perhaps there is no such thing as a neutral calcium phosphate?

M. Oh, yes there is. The neutral is the only one present in nature. You must double the formula of phosphoric acid, then you have 6H and can replace these with calcium.

P. Ah; so that's the way. I did not know we were allowed to do this. Then the neutral phosphate is $Ca_3(PO_4)_2$.

M. Correct. Now write the formulæ of the two acid phosphates.

P. That is easy enough when two hydrogen are replaced, I just need to insert one calcium instead: $CaHPO_4$. Is that right? But if only one hydrogen is to be removed I must again use the double formula. That would give me $Ca(H_2PO_4)_2$.

M. Quite correct. This last substance is the effective constituent in the superphosphates (p. 179), and is formed by the action of sulphuric acid on the neutral salt. What is the equation? Think a little first.

P. In order to take away two calcium I require two sulphuric acid, since the sulphate ion is dibasic; so

$$Ca_3(PO_4)_2 + 2H_2SO_4 = Ca(H_2PO_4)_2 + 2CaSO_4.$$

M. Very good. This acid salt, monocalcium phosphate, is soluble in water, and can therefore easily get access to the roots of plants, while the neutral compound is practically insoluble. That is why we convert the one into the other. The neutral phosphate is also found in the slag from iron ores (p. 178); indeed, this is the form most usual when an excess of base is present. It then requires no further treatment, as it disintegrates in the air into such a fine powder that it readily reaches the roots and becomes absorbed. That will be enough for to-day.

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28. CALCIUM II.

M. We need not go over what we said yesterday, since it was all quite simple.

P. There is something I would like to ask in reference to the decomposition and formation of calcium carbonate. You told me that, on heating, it broke up into calcium oxide and carbon dioxide; but these again unite to form the carbonate when mortar absorbs carbon dioxide from the air. These reactions are the very reverse of one another. Is the difference simply a matter of temperature?

M. Your supposition is quite correct; the temperature determines the result. Of course, the two cases differ slightly; in the first instance, calcium oxide is formed; but in the second, it is calcium hydroxide that changes into the carbonate. But, nevertheless, the point is one of considerable interest because carbon dioxide has to drive water out of the mortar.

P. Yes; so I see. Please explain how it does that.

M. Carbon dioxide bears the same relation to calcium carbonate as water vapour does to liquid water. Just as water has, at each temperature, a definite vapour pressure which becomes greater according as the temperature rises, so calcium carbonate has a certain carbon dioxide pressure which increases in proportion to the increase of heat.

P. Then the conditions during limestone burning must be somewhat comparable to those prevalent when water boils?

M. Quite right. If we heat calcium carbonate in a closed flask which is fitted with a manometer, we find that the mercury rises as the temperature is increased, so that a pressure of one atmosphere is obtained at 812°. Of course, we usually apply considerably greater heat so as to hasten the decomposition.

P. But what happens at the ordinary temperature?

M. Then the pressure is so slight that it cannot be meas-

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ured. Indeed, even at 440° it is only just appreciable. Air usually contains about 1/2000 of carbon dioxide, which thus exerts a pressure of 1/2000 of an atmosphere. And since this is certainly greater than the decomposition pressure of calcium carbonate at the ordinary temperature, the reaction therefore goes in the reverse direction.

P. Ah; now I begin to understand.

M. We can trace analogous conditions in other cases which lend themselves more easily to observation. You remember that sodium bicarbonate can be formed from sodium carbonate and carbon dioxide. (P. 210.) Conversely, the bicarbonate decomposes, under strong heat, into the neutral salt, carbon dioxide, and water. (P. 228.)

P. Yes; but in this instance the formation of the bicarbonate occurred in a solution.

M. That makes no difference, for the solid carbonate acts in the same way if we first dampen it with the water necessary for the reaction.—Now we come to the halogen compounds of calcium. You have already met with the chloride, $CaCl_2$.

P. I prepared it from calcium oxide and hydrochloric acid; it could only be obtained with difficulty in the solid condition.

M. That was because it is extremely soluble, and cannot, therefore, be easily freed from the last traces of water. It crystallizes with from 1 to 6 H_2O; and the solid salt deliquesces into a solution if left exposed to the air, so eagerly does it attract moisture. Therefore, it is used to dry gases and other substances. It has an advantage over sulphuric acid in not being corrosive and so can do no damage. However, it is not such a thorough desiccator.

P. You speak as if there were different degrees of dryness. If we say a jug is empty it cannot be more empty.

M. That is just the point. We cannot make it quite empty. Or, in plain language, we have no means of taking away the whole of the water vapour from anything. All we

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can do is to remove it down to a certain extent, which depends on the nature of the desiccator. Thus sulphuric acid manages to extract a little moisture from air which has been dried by calcium chloride, and this same air can give up a trace of water to phosphorus pentoxide; but, even then we ought not to assume that absolutely all the water has been removed.—Calcium chloride is of no other special importance. In many chemical industries, as, for instance, the ammonia-soda process (p. 227), it is allowed to go to waste as a worthless by-product.

P. And how does it compare with the bromide and iodide of calcium?

M. Both these resemble it in many ways. They deliquesce, and are of little use. On the other hand *bleaching-powder*, hypochlorite of calcium, is a very important substance.

P. I have heard that name before. It is a salt of hypochlorous acid.

M. Quite right. You remember that sodium chloride and sodium hypochlorite are formed by the action of chlorine on sodium hydrate. We can act on calcium hydrate in a similar manner. Write the equation, and recollect that calcium is divalent.

P. Then I must take a double quantity of chlorine:

$$2Ca(OH)_2 + 2Cl_2 = 2H_2O + CaCl_2 + Ca(OCl)_2.$$

M. Quite correct. But it is often written as follows:

$$Ca(OH)_2 + Cl_2 = H_2O + Ca\overset{Cl}{\underset{OCl}{}}.$$

P. Why is the last formula written that way?

M. To show that it is a double salt. The divalent calcium ion has one valency in combination with the monovalent chlorine ion, the other with the monovalent hypochlorite ion. Up till now I had no opportunity of showing

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you an example of the two different methods of writing formulæ. It is because both varieties are in use that I explain them to you now. Do you remember why bleaching-powder is manufactured on a large scale?

P. Yes. Chlorine-gas is not suitable for transport, and to make it so, they must convert it into some solid compound which will easily give it up again.

M. And how do they make bleaching-powder part with its chlorine?

P. By an acid treatment.

M. Yes. Write the equation with sulphuric acid, and use the second formula.

P. $Ca\overset{Cl}{\underset{OCl}{}} + H_2SO_4 = CaSO_4 + H_2O + Cl_2$.

We obtain just the same quantity of chlorine as was put in.

M. Right. This is a good way of making chlorine for laboratory purposes. We use the apparatus we took for the preparation of hydrogen sulphide (Fig. 22, p. 150), and allow concentrated hydrochloric acid to drop in from the funnel.

P. What advantage has this over our old method of preparing it from manganese dioxide and hydrochloric acid?

M. Only this: no heat is required. Therefore, it is simpler and quicker. Let us now leave bleaching-powder and turn to another calcium compound of still greater industrial importance, glass. I have already told you its composition.

P. It is a silicate, but I do not know of what metal. It contains sodium, I believe.

M. Ordinary glass consists of the silicates of sodium and calcium. It is prepared by heating together sodium carbonate, quartz-sand, and limestone. Carbon dioxide is given off and the two silicates are formed. These fuse at a great heat into a water-clear liquid.

P. How does the silicic acid manage to displace the carbonic acid? I remember well how you yourself told me

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that all over the earth's surface the silicic acid is being expelled by the carbonic acid.

M. You are quite right. The fact is that the latter reaction takes place at the ordinary temperature; but the reverse occurs under great heat, because silicic acid is not volatile, and carbonic acid is.

P. I think I understand. It is as we have seen before; the slight quantity of carbon dioxide displaced escapes, and so more can be driven out; this process is repeated until no more is left.

M. Quite correct. We have already often had occasion to adopt this theory, and its application will help us to elucidate many another reaction. But to return to glass; the mixture is first gently heated to drive off the carbon dioxide, for otherwise this would throw the molten mass out of the crucible, and then the temperature is raised as high as possible so that all bubbles of gas may escape and any impurities settle to the bottom. We can either mould the liquid mass into what we require, or let it cool until it becomes partially solid, and then blow the glass. This latter process is the one most usually adopted.

P. I do not understand how you can "blow" it.

M. The ductile glass can be blown into shape just as we make soap-bubbles. Only we are able to make the former take and, by cooling, retain any desired shape, while a soap-bubble is always spherical.

P. Please tell me how they do this.

M. To make window-panes, for example, they first blow a ball. This they wave to and fro and so manipulate that it takes the form of a cylinder with round ends. These are cut off, the cylinder is slit from end to end, and we then only require to spread it flat in order to have a square sheet. However, all this is much better seen than described. Be sure to accept any opportunity you may be offered of going over a glass factory. The laboratory glass-blower, with his bellows

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and gas-jet, works in exactly the same way, only on a much smaller scale; and you will often get a chance, at the annual fairs, of watching itinerant followers of this art. They can make their glass tubes assume almost any shape you please.

P. Yes; but how are the tubes made?

M. Very simply. One man blows a ball; another, using iron tongs, sticks a lump of glass onto the opposite end; and then both run in different directions. The ball stretches out into a long elliptical shape and the centre becomes a tube, which is all the finer the faster the men have run.

P. A ball is always the first thing formed; and soap-bubbles, also, are round. Why is this?

M. It is caused by the surface tension. The surface of all liquids has an active tendency to become as small as possible. Now a circle provides the smallest surface for a given volume. The other shapes obtained in glass-blowing are subject to this effect, only in a degree modified by the force of gravity and the change in the ductility between warm and cold glass.—Let us now conclude for to-day. I have practically said all I had to say about calcium.

P. Pardon me if I ask you something else. Has the calcium carbide, which I buy for my bicycle lamp, got anything to do with calcium?

M. Certainly. It is, as the name implies, a compound of calcium and carbon. It is obtained by heating lime with charcoal: $CaO+3C=CaC_2+CO$. Read the equation.

P. Calcium oxide and carbon give calcium carbide and carbon monoxide. Then would I be able to make some myself?

M. No; you would not. For the temperature required is so high that it can only be obtained in an electric furnace. Do you know how the illuminating-gas is obtained from it?

P. Yes; with water. The lamp is constructed so that the light can be regulated by allowing water to drop onto the carbide.

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M. Right. The reaction is:

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

The gas has the composition C_2H_2, and is called acetylene. It, also, is a hydrocarbon (p. 190), but contains much less hydrogen than the others of which I told you.

P. Why does it burn so brightly?

M. Principally because it contains very much more energy than its elements. The heat of combustion of 2C is 812 kj., that of 2H is 286 kj., their sum is 1098 kj.; while acetylene, on the other hand, produces 1321 kj., on burning.

P. May I calculate how much energy is absorbed when acetylene is formed? I took good note of how these calculations were made: (P. 189.)

$$\begin{array}{l} 2C + 4O = 2CO_2 + 812 \text{ kj.} \\ 2H + \ O = \ H_2O + 286 \text{ kj.} \\ \hline C_2H_2 + 5O = 2CO_2 + H_2O + 1321 \text{ kj.} \end{array}$$

Consequently

$$2C + 2H = C_2H_2 - 223 \text{ kj.}$$

Therefore, 223 kj. were used up. But why should this cause the gas to give a strong light?

M. Because, since so much more heat is produced by its combustion, the temperature is raised to a correspondingly high degree. You know that the greater the heat of a substance the more light will it emit.

P. I never thought that these calculations would enable me to explain so many things; I am, therefore, all the more pleased that I managed to understand them.

M. This shows you why a very great quantity of energy must be expended in the preparation of calcium carbide; we have to employ a strong current to heat the furnace.

P. And this energy is afterwards given out as light. So then we might really call this electric light!

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M. No; that would not be correct. The energy of the electricity is first all changed into heat; and a part of this is converted into chemical force. What is stored up in calcium carbide is altogether of a chemical nature.

P. I see. Once energy is converted into another kind, this is quite distinct from the former variety.

M. That is right. Here we will leave calcium.

29. BARIUM, STRONTIUM, MAGNESIUM.

M. You remember what I told you about the relationship between the three elements chlorine, bromine, and iodine?

P. Yes. Their properties are similar to one another, but are graduated according to the progression of their combining weights.

M. Well, the alkali metals behave in the same manner. Of these you have met with potassium; and there are two more, which act analogously and are very rare. They are rubidium and cæsium. Again, there are three very similar metals of the alkaline earths, calcium, strontium, and barium. Let me draw up a small table of combining weights to show you how comparable these three groups are.

Chlorine.....	35.45	Bromine.....	79.96	Iodine.....	126.85
Potassium....	39.15	Rubidium....	85.4	Cæsium.....	132.9
Calcium.....	40.1	Strontium....	87.6	Barium.....	137.4

P. Yes. The numbers in each column closely approximate, and the differences between the atomic weights of analogous elements is, in each case, about 45. Why do these figures not coincide more closely? Perhaps they are not correct?

M. On the contrary, we know for certain that they are accurate to one unit. These irregularities really exist; but we do not yet know why they are there, or what causes them.

P. Can we tabulate all the elements in this manner, or does this system apply only to a few?

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M. We can arrange them all according to their combining weights, and thus obtain a fairly regular table, but the full significance of such a formation would not appeal to you until you have made a complete study in detail of the individual members.—What do you already know of barium?

P. Practically nothing; except that it is a test for sulphuric acid, i.e., for the sulphate ion. It forms an insoluble precipitate, $BaSO_4$.

M. Correct. So you see from this formula that the barium ion, $Ba^{\cdot\cdot}$, is also divalent. It is colourless, but differs from the calcium ion in being poisonous. Metallic barium is little known, it is yellowish, has properties similar to those of calcium, but oxidizes quicker and more easily. The hydroxide, $Ba(OH)_2$, is much more readily soluble in water than calcium hydroxide, and the solution is known as *baryta water.* Barium is found in nature principally as the sulphate, $BaSO_4$, which is called by mineralogists *barytes* or *heavy spar.*

P. Why heavy spar?

M. Because it has an unusually great density. Its specific gravity is about 4, whilst that of most of the non-metallic minerals is 2 or 3. The name barium is derived from a Greek word meaning "heavy." Barium sulphate is very inactive; it does not dissolve in acids, nor is it affected by any of the constituents of the air or by moisture. The artificially prepared salt is therefore used as a white pigment, and is known, on account of its wearing properties, as *permanent white.* The carbonate, $BaCO_3$, is found in nature as *witherite.* It is the source of most of the artificial salts of barium. The chloride, $BaCl_2$, forms shining crystals with $2H_2O$, and is familiar in the laboratory as a test for the sulphate ion. The nitrate, $Ba(NO_3)_2$, crystallizes as a water-free salt, and is only slightly soluble. It is used in fireworks because it burns with a green flame.

P. And have the other barium compounds this property?

M. Yes; all of them; but not in the same degree. The

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nitrate gives the best practical result. The same thing applies to strontium, for its nitrate is used to give a red flame. This metal is very similar to calcium and barium. It is yellowish, and oxidizes easily in moist air. The hydroxide, $Sr(OH)_2$, is white, and is more difficultly soluble in water than barium hydroxide, but more easily than calcium hydroxide. Its monoxide, SrO, is called *strontia*.

P. How did it get its name?

M. From the parish of Strontian, in Scotland, where certain minerals which contained it were first found. These natural compounds are (just as was the case with barium) the sulphate, $SrSO_4$, and the carbonate, $SrCO_3$. The former is called by mineralogists *celestine*, as it is sometimes sky-blue owing to the presence of extraneous matter; the latter is known as *strontianite*.

P. Why have all these substances different names in mineralogy and chemistry?

M. Partly because we became familiar with the minerals first before we had investigated their composition, which was often found to be so complicated as to be incapable of affording us any simple chemical designation. Therefore, we had to invent some name which would at least have the advantage of being short.

P. Who decides what a mineral is to be called?

M. This right is generally granted to whoever first finds and describes it.—Strontium sulphate, as well as the carbonate, is apparently insoluble in water, i.e., it dissolves in extremely minute quantities. In this respect, it stands between barium sulphate and calcium sulphate. The chloride and the nitrate both dissolve easily.

P. Are the strontium compounds of much practical use?

M. No; of very little, except, as I said, to produce a red flame. The hydroxide plays a part in sugar refining, but I cannot enter on that question now.—These two elements are not actually rare, but still they are not found in nature

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in any large quantities. However, they are more abundant than bromine and iodine.—Lastly, we come to a very common metallic earth, magnesium. It bears the same relation to calcium as sodium does to potassium.

P. Do their combining weights show this?

M. Certainly. Sodium has 23.05 and magnesium 24.36; both nearly approximate, as do those of calcium and potassium and the other two pairs on our table. There is another peculiar similarity, namely, that magnesium, in some measure, stands rather further apart from calcium than the latter does from strontium and barium; just as sodium may be said to have less in common with potassium than the latter has with rubidium and cæsium.

P. I do not understand that. On the contrary, the combining weights would make us infer otherwise, since the interval is less.

M. Yes; but the properties of the elements and their corresponding compounds are what we have to consider. Sodium, for example, does not catch fire on coming in contact with water, while potassium, rubidium and cæsium do. Magnesium has almost no action on water, while calcium, strontium and barium quickly decompose it.

P. Yes; I remember that, for I am already fairly well acquainted with magnesium. We made many of our previous experiments with it. We used it as a test for acids.

M. Quite right. This test depends on the fact that the metal has only a very slight effect on water, but gives a distinct reaction with acids. Calcium, also, acts much more strongly on acids than on water, but as both reactions are vigorous, the difference is not so clearly visible.—To what use do we put magnesium?

P. To produce a bright light. Magnesium ribbon burns with a blinding, white flame, and photographers use the powder to make a strong flash.

M. Yes. Magnesium has a great heat of combustion,

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602 kj., and, therefore, the oxide is formed at a very high temperature; but in spite of this, it neither melts nor vapourizes, another fact which conduces to the production of a strong light.

P. How is that?

M. Because a solid body, as a rule, gives out more light than a liquid or a gas at the same temperature. I melt a little clear glass in the loop of my platinum wire (p. 217); the solid platinum glows brightly, while the liquid glass throws out no light at all, but remains as transparent and dull as at the ordinary temperature, although it is just as hot as the wire.

P. How remarkable! Had I not seen this I would never have believed it.

M. Substances which let light pass through them can emit none. Let us take some dark-blue or dark-green bottle-glass instead of the colourless variety. Now you see that this glows like the platinum, but not nearly so brightly. On being heated it can give out its light, because all is absorbed and none is allowed to pass through.

P. May that be regarded as a universal rule?

M. Certainly. However, you will learn more about this in physics.—You already know the appearance of the magnesium oxide which is produced by the combustion of the metal.

P. Yes; it is a white substance, soluble in acids.

M. It has the formula MgO, and is called *magnesia*. It unites with water, forming the hydroxide, $Mg(OH)_2$, but does not react nearly so violently as lime; hardly any increase of temperature is appreciable, and if the magnesia has been strongly heated, the combination is too slow to be detected at all. Magnesium hydroxide is almost insoluble in water, but if we lay a piece on some red litmus paper and moisten with a drop of water a blue stain is produced. It dissolves easily in acids and forms salt solutions which contain the

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colourless, divalent magnesium ion, $Mg^{\cdot\cdot}$. Since all these salts have a bitter taste we may ascribe this property to the magnesium ion.

P. Then the sour taste of acids is the property of the hydrogen ion?

M. Quite right. Of the magnesium compounds the sulphate is well known. It dissolves readily in water, crystallizes with $7H_2O$, and usually goes by the name of *Epsom salts* or *bitter salt*.

P. Has it also a bitter taste?

M. Certainly. It is present in many mineral springs. These are sometimes called bitter-waters and, like Glauber salts, have an aperient effect.—I have already mentioned magnesium chloride, $MgCl_2$, when speaking of potassium chloride, with which it forms the double salt *carnallite* of the composition $KCl \cdot MgCl_2 \cdot 6H_2O$. This is found in the earth, and by a special process of crystallization we can eliminate from it the magnesium chloride, which is of little use and is generally allowed to run to waste into the streams.

P. Is it not poisonous?

M. No; all springs and river-water contain magnesium ions, more or less. It only becomes harmful if present in large quantities. The most widely spread of all the magnesium compounds is the carbonate, $MgCO_3$. It is known to mineralogists as *magnesite*. It resembles limestone, with which it forms a double salt, called *dolomite*, $CaCO_3 \cdot MgCO_3$. Many great mountains are formed of this mineral.

P. I think I have read somewhere of the Dolomites.

M. This is the name given to a range of hills in the south of Tyrol. The weathering effect causes dolomite to assume peculiarly jagged and rugged forms, and these add a characteristically striking beauty to the scenery of those mountainous tracts. On heating, magnesium carbonate readily parts with its carbon dioxide and changes into the oxide. If we

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try to prepare the carbonate by acting on a magnesium salt with the carbonate of potassium or of sodium, we do not obtain the pure compound, but a mixture of the hydroxide with it.

P. Why is that?

M. You know that a carbonate of the alkali metals in solution is partially split up by the water, and therefore colours red litmus blue, because it contains the hydroxyl ion. (P. 211.) So when the magnesium ion is brought in contact with such a solution it is thrown down as the hydrate and also as the carbonate, since both these products are difficultly soluble in nearly the same degree.—The precipitate is in the form of a white, very light powder which is known in pharmacy, as a medicine, under the name of *magnesia alba*, i.e., white magnesia.

P. It is useful in cases of stomach-ache.

M. Ah; I see you sometimes have to take some! In conclusion, let me give you the names of some minerals which consist of magnesium silicate in combination with water of crystallization: *talc*, *steatite* or *soapstone*, and *serpentine*. Just take them in your hand; they all feel peculiarly smooth, almost greasy. They can stand a very high temperature, and therefore serve, especially the steatite, as gas-burners.

30. ALUMINIUM.

M. After the metals of the alkaline earths we come to the metallic earths. We shall study only one of these, because the others are so rare that we have not been able to find out much about them. Their ions are trivalent and their hydroxides are weak bases. The best known is aluminium; you have already seen this.

P. Yes; often. It is beautifully white, like silver, but seems to be pretty soft.

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M. Quite right. It is by no means a noble metal, for though it resists the air fairly well, still it is easily attacked by salt solutions of all kinds. Its durability on exposure to the atmosphere is due to the fact that it becomes coated with a thin skin of oxide which, being transparent, is therefore invisible and protects the metal as a varnish would.

P. But what if this became cracked or stripped off anywhere?

M. Then a fresh layer of oxide would form there spontaneously. But I will show you how we can make this protection prove ineffectual. Here is some sheet aluminium. I place a drop of mercury on it and rub with a rag moistened with hydrochloric acid—

P. The mercury is making it shine like a looking-glass.

M. Look closely.

P. What is the reason for this abrupt change? A sort of haze is forming over the bright part; it increases so rapidly that my eyes can scarcely follow its course. I never saw anything like that before!

M. Aluminium hydroxide has been produced on the metal by the action of the atmospheric moisture; but it cannot form a firm coating on the liquid surface where the mercury is, and so further oxidation proceeds there very fast. Feel the other side of the sheet; it has become quite warm. We must, therefore, take special care what we are about when aluminium is in the presence of mercury. Since aluminium unites so readily with oxygen much energy is required to prepare the metal from its oxide. We manage this by electrolyzing the fused compound; the aluminium travels to the cathode, the oxygen to the anode, which, being made of carbon, immediately burns the oxygen to carbon dioxide and thus facilitates the decomposition. Aluminium has a density of 2·7. It is, therefore, much lighter than the ordinary heavy metals, which are at least three times its weight. It can be beaten into fine wire or foil. The latter is often used for

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"silvering," since it preserves a better lustre and is not coloured black by hydrogen sulphide as genuine silver-leaf is. (P. 132.) It is used for similar purposes as a finely ground powder, known as *aluminium bronze.* Aluminium is attacked and dissolved by acids. Just write the equation with hydrochloric acid, and remember that this metal is trivalent.

P. $Al+3HCl=AlCl_3+3H$. Is that correct?

M. Yes. The solution contains the colourless aluminium ion, $Al^{\cdots}$, which unites with anions to form salts. But these, when dissolved, resemble the carbonates of the alkali metals and are partially split up by water into the acid and hydrate, because aluminium hydroxide is a weak base. In the case of the alkali carbonates the acid is weak, and therefore their solutions have a basic reaction; in this case the base is feeble—

P. And, therefore, aluminium salt solutions give an acid reaction. May I see if they do?

M. Here is a little solid aluminium chloride. Just dissolve it in water.

P. Yes; it makes blue litmus paper red in a second. How does water manage to exert such contrary effects?

M. Water contains a very small quantity of hydrogen ion, $H^{\cdot}$, and hydroxyl ion, OH', for it breaks up thus:

$$H_2O=H^{\cdot}+OH'.$$

Therefore, it can act as an acid and as a base. But since both varieties of these ions are present only in extremely slight quantities their action is only effective on the salts of such acids or bases as are very weak. That aluminium chloride really does dissociate when dissolved in water is clear from the fact that the salt cannot be obtained again by evaporation. Any attempt leads to the following reaction:

$$AlCl_3+3H_2O=Al(OH)_3+3HCl.$$

Read it!

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P. Aluminium chloride and water give aluminium hydroxide and hydrogen chloride. Then, could we make hydrochloric acid in this way?

M. Yes; we could; but the aluminium chloride, besides being expensive, would first of all need to be prepared by acting on aluminium with hydrochloric acid:

$$Al + 3HCl = AlCl_3 + 3H.$$

It is then obtained as a white substance which, on warming, volatilizes. It dissolves in water with great evolution of heat. If we treat the solution with ammonia, aluminium hydroxide is thrown down.

P. It is difficult to see this precipitate; it seems transparent and like gelatine.

M. It is amorphous. The normal hydroxide, $Al(OH)_3$, is found in nature as *hydrargillite*, and in various degrees of dehydration as

bauxite, $2Al(OH)_3 - H_2O = Al_2O_5H_4$;
diaspore, $2Al(OH)_3 - 2H_2O = 2AlO_2H$;
and *corundum*, $2Al(OH)_3 - 3H_2O = Al_2O_3$.

Bauxite is important as the raw material from which the metal is prepared. On heating, it parts with its hydrogen as water and changes into aluminium oxide. Corundum forms crystals, distinguished for their great hardness. The granular varieties, which are usually coloured dark by iron oxide, are known as *emery*. This is very effective for grinding or polishing glass and steel.—I shall now show you a peculiar property of aluminium hydroxide. I have here a solution of the chloride. If I carefully add a little caustic potash a precipitate is formed. What is it?

P. $AlCl_3 + KOH$—no, I will have to take three times as much—

$$AlCl_3 + 3KOH = Al(OH)_3 + 3KCl.$$

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It must be aluminium hydroxide; and, indeed, it looks as if it were.

M. Yes, that is so. But if I now add more potassium hydrate the precipitate dissolves and we obtain a clear solution.

P. I do not understand that.

M. I could not expect you would. Aluminium hydroxide can act not only as a base but also as an acid; for it contains some hydrogen which enables it to behave as a weak acid. It thus resembles water, but is stronger in its basic than in its acidic properties. The solvent effect may be accounted for by the fact that the aluminium dissolves in the caustic liquor with an evolution of hydrogen. Here is the mixture in a test-tube; if I warm it a gas is at once given off. You can make the experiment afterwards, and convince yourself that the gas really is hydrogen.—The oxide of aluminium is known as *alumina*, and the silicate (which forms the basis of the various *clays*) is present in nature in combination with other silicates, which become decomposed by the action of carbon dioxide and water (p. 200), while the aluminium silicate remains unaltered. Aluminium hydroxide is so weak a base that the feeble carbonic acid cannot manage to unite with it. In fact, aluminium carbonate has never been known to exist. And so the silicate of aluminium is carried away as a fine powder by the streams and rivers and deposited in quiet waters. According as the clay is more or less pure it is known as *porcelain-clay*, *potter's clay*, *loam*, and also as *marl*. The principal impurity in the latter is calcium carbonate, and in the others quartz-sand and oxide of iron.

P. Please tell me how they make porcelain cups and saucers.

M. They first fashion the form they wish from the purest clay; let it dry; and "burn" or "fire," i.e., heat it. It is then dipped into a milk made of finely ground felspar and

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water; the latter is absorbed, while a thin, uniform coat of felspar remains over the surface.

P. What is that for?

M. Felspar is a compound of the silicates of potassium and aluminium. It melts at a high temperature, but more easily than clay, into a shining liquid which, when the "firing" process is repeated, soaks into and leaves a varnish over the still solid clay. This gives the glazed, polished appearance to porcelain.

P. How is it so beautifully smooth?

M. Because of the effect of surface-tension. A smooth surface occupies less space than a rough one, and therefore all liquids assume the former condition if left undisturbed.

P. Yes; so they do. But I never thought of so simple an explanation.

M. I will now tell you how they proceed with the other kinds of pottery. Earthenware is made from clay of great fire resistance, it is heated strongly and given a glaze by introducing ordinary salt when the oven is at its hottest. A reaction ensues between the water vapour present, the sodium chloride, and the clay; hydrogen chloride is evolved and a double silicate of sodium and aluminium is formed.—Delf is not fired at so high a temperature. The dried ware is first covered with a powder, and this, during the burning, melts into a glass (p. 240), which gives the smooth, polished appearance.

P. What effect does the firing have on the clay?

M. It drives off the water and makes the pottery dry together into a compact mass. This is porous, but will hold water, which, on the other hand, soon causes the unburnt material to crumble to pieces. During firing the clay decreases in bulk, the more as the heat is raised. This shrinkage has to be taken into account if we wish to make a vessel according to a certain definite size.

P. Why are bricks and flower-pots generally red?

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M. Owing to the presence of iron oxide in the clay. The various colours in pottery are produced by metallic oxides. Later on we shall see what colours are peculiar to the individual metals. The opaque, white crockery for ordinary table use is prepared by the addition of bone-ashes to a vitreous mixture in which calcium phosphate cannot dissolve, but retains its solid condition. A material of similar nature is also used to coat or "enamel" ironware.

P. I would like to go much more deeply into these matters.

M. You can make a detailed study of them later on, for there is a special department of science, technical chemistry, which deals with such subjects. I only touch on them so far as they affect general chemistry in order to show you how much the different branches of science dovetail and are interdependent on one another. But, as a rule, in order to thoroughly understand any technical process we must have a wide knowledge of chemistry; so we shall leave these cognate matters on one side for the present.

P. I suppose this subject must be a most interesting one.

M. To be sure it is.—This salt, here, is aluminium sulphate. Just see if you can write its formula.

P. Sulphuric acid has two hydrogen, and aluminium is trivalent; but that does not give me an equivalent. So I must take three sulphuric acid, which will equal six hydrogen, and therefore I require two aluminium. Is that correct? Then the formula is $Al_2(SO_4)_3$.

M. That is right. This subtance crystallizes with $24H_2O$. Its solution, if shaken with a saturated solution of potassium sulphate, yields a powder, like sand. Examine it with the microscope.

P. It consists of beautifully clear, regular crystals.

M. It is a compound of the sulphates of potassium and aluminium, and therefore is what is known as a double salt. The formula is $K_2SO_4+Al_2(SO_4)_3$, or more simply $KAl(SO_4)_2+12H_2O$, which represents the first divided by

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two, with the addition of the water of hydration. In this last formula we can consider that one of the four hydrogen (of the two sulphuric acid) is replaced by the monovalent potassium, and the other three by the trivalent aluminium. This salt has been known for a long time. It is called *potassium alum*, or simply *alum*, from the Latin *alumen*.

P. Whence we also obtain the name aluminium?

M. Quite right. I tell you these derivations so that you can trace out your own deductions from them. For long, alum was the only salt of aluminium which we knew how to prepare in the pure state.

P. Why was that?

M. Because all these salts crystallize very badly, and crystallization is almost the only means of obtaining them in a pure condition if we have to start from a contaminated source. In the dyeing industries, aluminium compounds are used as *mordants*.

P. What are they?

M. Many colouring-matters do not combine firmly with thread or cloth fabrics, but they do with aluminium hydroxide, which, in its turn, unites with the material to be dyed. Thus the colours are held fast to the cloth by the instrumentality of the aluminium hydroxide. I cannot satisfactorily explain the reason of this because you are not yet far enough advanced.

P. But alum is not aluminium hydroxide. Can this be extracted from the salt by the cloth?

M. The explanation lies in the fact that the hydrate is a very weak base; and therefore a watery solution of the salt is partially hydrolyzed, i.e., split up by the chemical action of the water, into the free acid and free base. (P. 252.) In this way the cloth can seize on a portion of the aluminium. How could we increase the dissociating effect of the water? On what does this depend?

P. The base or the acid must be feeble. But surely

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we cannot make the hydroxide more feeble than it already is?

M. No; but it is not absolutely necessary to have sulphuric acid; we could use the aluminium salt of a weaker acid. Can you suggest one?

P. Yes; a whole number. Hydrogen sulphide, carbonic acid, boric acid, acetic acid, phosphoric acid.

M. Only one of these, namely, acetic acid, forms a soluble aluminium salt. I have here a solution of alum. I bring it to the boil, it remains clear. Now I add a little sodium acetate; a cloudiness soon appears. It is caused by some aluminium hydrate being thrown out of solution. The aluminium acetate present has been split up by the water to such an extent as to yield this precipitate.

P. But it is possible we may have no aluminium acetate in the solution, but aluminium sulphate and sodium acetate. How do we arrange so that aluminium acetate is formed?

M. There is no necessity to arrange anything. You know that in a salt solution the ions are mingled together, but are, to a large extent, independent of one another. Well, here we have the aluminium ion (obtained from the sulphate) and the acetate ion (obtained from the sodium salt) exactly in the same condition as if we had only taken solid aluminium acetate and, by solution in water, split it up into its ions.

P. Again, its very simplicity has prevented me from grasping the situation.

M. I hardly expected you would grasp it, because our former experiments tended to give you the impression that the ions acted selectively. As, for example, whenever the chlorine is brought in contact with the silver ion, or the barium with the sulphate ion, a precipitate is produced.

P. So, then, in order to obtain a solution of a salt I only require to bring its ions together by dissolving them, no matter from what and with what compounds they are obtained.

M. Quite right; or more accurately: you then have a

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solution which behaves in just the same manner as a solution of each respective salt. I must, however, add that in some few cases we meet with deviations from this rule; yet in every one of these instances we have been able to prove that our theory was not at fault, but that the ions, which we supposed were present, had no existence in fact.

P. What becomes of them then?

M. They are changed into other compounds. We cannot enter further into this question now, because you would not be able to follow the explanation. I have only brought this point to your notice so that you may be prepared for future instances. That will do for to-day.

31. IRON I.

M. We now enter on the study of the heavy metals; and we commence with iron, the most important.

P. Why should this be the most important? I thought that gold was.

M. Because, I suppose, gold is one of the dearest, and iron one of the cheapest. That is just the reason why the latter is so much more valuable than gold.

P. I do not understand.

M. If iron were as expensive as gold we could not think of using it for machines, railways, bridges, and the numerous contrivances available to the manufacturer of the present day. All the gold in the world would not suffice for the requirements of one moderate-sized engineering establishment.

P. I now grasp your meaning. But still I cannot quite see why such a common substance should be of such value. Surely a thing is valuable only because it is scarce.

M. You are confusing two different ideas. What can be more valuable than oxygen or sunshine? Life would cease the moment we had neither one nor the other. And yet both

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cost us nothing; they are bestowed by nature with ungrudging hand. They are of inestimable value; but we would not call them costly, as we would such things as are only found in small quantities, for instance, gold and precious stones. Their importance lies in the fact that they can be used as equivalents of other objects of worth, such as fields, herds, woods; and, as they are proportionately light and small, they are easy to keep and carry about as a means of barter for bulkier material. This, of course, is the principle on which the currency of all civilized countries is based. —Therefore, iron is valuable and important chiefly because it is so abundant.

P. But I have never seen any natural iron. Does it lie deep in the earth?

M. It is scarcely ever found in the free state; but its compounds, from which we prepare it, are spread far and wide. What is the colour of the ground and rocks in places where no plants have found a lodging?

P. Sand is yellow; stones are brown and reddish, often grey and greenish.

M. Yes. Well, all these colours are caused by iron. For you know that the silicate compounds of aluminium, calcium, and magnesium (which form the greater portion of the earth's crust) are colourless.

P. To be sure. I never thought of that.

M. Therefore, if stones, and soil which is made from them, are coloured, it must be due to some other element; and this other element is nearly always iron, for it is so wide-spread. However, the black and brown soils, which bear vegetation, obtain their tint from carboniferous matters produced by the decay of plant remnants. We speak of this as *mould*, but the name does not imply that it is a definite chemical compound.

P. Do we make iron out of these yellow and brown stones?

M. No; they do not contain sufficient; but in certain

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portions of the earth we find iron ores which yield so much of the metal that it pays to work them. Most of these compounds are oxides of iron; I shall describe the method of preparation later on. In the first place, tell me what you know of iron itself.

P. It is grey and very ductile. It rusts on exposure to the air.

M. Good. Iron may be distinguished as *cast iron*, *wrought iron*, and *steel*.

P. What is the nature of these varieties? Are they allotropes, as in the case of carbon?

M. No. All iron contains carbon, and these different kinds depend on the proportions present. Pure iron resembles wrought iron, but is a little softer. It is grey and ductile. Wrought iron contains less carbon than the other commercial varieties, less than one hundredth part. What is a forge? Have you ever watched a blacksmith at work?

P. Yes. He first makes the iron red-hot, then it becomes pliant, and he can bend and hammer it into whatever shape he pleases. It hardens again on cooling.

M. Right. Before iron melts it first softens. In this it differs from most solid substances. Ice, for example, does not soften at the melting-point, but becomes brittle, sulphur does the same. Therefore, we can make two rods of iron unite into one piece by hammering them together when hot, as if they had been two lumps of rosin or wax. This process is called *welding*.

P. Yes; I have seen it done. The blacksmith told me it required much greater heat.

M. Quite correct; so it does. Now, let us take cast iron. Have you ever carefully examined any?

P. Yes. It is greyer than the other varieties and seems more easily broken, for we cannot bend it.

M. Right. It is neither ductile nor pliant. If you examine the broken surface of a piece of cast iron with the microscope

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you will notice that some of the crystals are bright, others dark. The latter are of carbon, in the form of graphite.

P. How does this get there?

M. Iron is produced from its ores by fusing them with charcoal, which dissolves in the molten metal to a saturated solution. But the iron, on solidifying, cannot retain so much carbon and the excess separates out in crystals.

P. What a pity these are not diamonds!

M. If we cool the iron solvent very suddenly we obtain diamonds, but they are so minute that it is difficult to recognize what they are. This graphite is dispersed throughout the cast iron in small leaves which destroy its homogeneity and render it more liable to fracture than wrought iron, since the latter contains none. I pour hydrochloric acid over some pieces of cast iron. What will happen?

P. The iron will dissolve, as the zinc did; the chlorine will combine with the metal and hydrogen will be given off. It effervesces, so it must be as I said.

M. Just smell!

P. Phew; how nasty! What is it? It smells something like hydrogen sulphide.

M. Cast iron contains a portion of its carbon in chemical combination with the metal. This carbon unites with the hydrogen and forms hydrocarbons (p. 190) of a disagreeable smell. If we burn the impure hydrogen a small quantity of carbon dioxide is found in the water produced. The graphite, on the other hand, is left behind as a black powder after the acid has dissolved all the iron.

P. Then we had better filter off the liquor from this residue.

M. Yes; do so. Now, if we cool the solution of carbon in iron very quickly we obtain quite a different form of cast iron. It has a white appearance, is extremely hard and brittle, and can be smashed into pieces which show a smooth, polished, crystalline break. Therefore, this is called *white cast iron* or *specular iron.*

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P. What causes this variation?

M. Owing to the extreme rapidity of the cooling the carbon has no time to separate out, but remains in combination with the metal; therefore, specular iron possesses the properties of iron carbide, and consequently, on dissolving in acids, gives off much more hydrocarbon than the grey iron. If we let cast iron solidify in metal moulds so that the heat is rapidly conducted away, a layer of white iron forms over the outside, while underneath it we have the grey variety, owing to the slower cooling in the interior. A cast thus prepared has the advantages of both varieties; it is as hard outside as the white, and yet, on the whole, is not so fragile, because of the soundness of the interior grey iron. Such a combination is known as a *chilled casting*, and is used for rollers, armour-plates, etc. Cast iron contains about 4 per cent of carbon.

P. And what is steel?

M. It is an iron containing from 1/2 to 2 per cent of carbon, according to the purposes required of it. Steel possesses in a most remarkable degree the hardening property, of which I have just spoken. Here is an old watch-spring; you see I can bend it up and it flies back again to its former shape.

P. We call that an elastic effect, do we not?

M. Yes. I heat one end of the spring and pass the glowing steel into water. Now try and bend it.

P. It breaks.

M. Yes; but it has become so hard that it will scratch glass. Just see if the sharp edge of the broken piece cuts this glass.

P. It does. But the steel in its previous condition does not.

M. Such steel which has been thus hardened by a sudden cooling from a red heat is called *chilled steel.* I now heat this chilled piece, but do not this time quench it in water. Examine it!

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P. It is quite soft, like lead. It is not elastic, for it can be bent crooked; nor does it now scratch glass.

M. However, if I again make it red-hot and plunge it into water it becomes hard and brittle as before.

P. So I see. But how did they make the steel elastic, as it was at first?

M. It is first hardened and then "tempered" by being cautiously raised to a certain temperature. It becomes less hard and brittle the greater the heat; so the elasticity can be regulated to any desired degree.

P. And how did they find out the exact temperature?

M. That was a matter of some difficulty; nevertheless, they found a means of solving it long before thermometers were thought of. I hold one end of the polished spring in the flame until it becomes red-hot, then allow to cool. What appearance has that portion intermediate between the heated and cold parts?

P. It is of various colours. I know you obtain the same effect if you heat the tip of a penknife.

M. Yes; and it won't have much of a point left! A regular and invariable succession of definite colours is always formed. Tell me what they are, beginning at the cold end.

P. Yellow, brown, red, purple, violet, blue, and grey.

M. This sequence is the result of different degrees of temperature. If we heat a piece of hardened steel so that it becomes yellow its temperature is not so high as it would have been had we warmed it until it turned blue. It is thus that we are able to judge of the temperature obtained, and each colour corresponds to a definite degree of hardness.

P. What a good dodge! And they knew all about this long ago?

M. No. They only knew that a certain hardness was reached on heating to a certain colour. For tools used for working on iron we let the hardened steel become yellow.

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For brasswork we require a brown, for woodwork a blue steel.

P. And for clock-springs a violet colour, such as this piece shows. But what causes this variation of tint?

M. Any very thin films will give these colours. I heat one end of a small glass tube until it falls together, and then blow a bulb with all my strength—

P. Hurrah! What a bang! You have blown the ball into clear, flimsy shavings. They are very pretty and like mother-of-pearl.

M. There you see what I mean. These colours in the thin glass are the same as those which invariably appear on a soap-bubble or any transparent substance which has become greatly attenuated. Physics will teach you why this is. On heating the polished steel the iron unites with oxygen and produces a layer of iron oxide, which thickens as the heat is raised. Now, the colour varies with the thickness, and therefore depends on the temperature.

P. I understand. But the layer would become denser were we merely to keep the steel at the same temperature, only for a longer time.

M. Certainly. But the metal would also become softer; so the ultimate result is the same.

P. Ah! That brings me to a question I wished to ask. Why does this process make the steel softer?

M. It is the case of the cast iron over again. At a high temperature iron and carbon unite to form a hard compound. If we apply quick cooling this carbide remains as such, and we obtain a hard steel. If a slow cooling is adopted, the carbide decomposes into iron and graphite, both of which are soft. On cautiously warming the hard steel again the conversion of the carbide into carbon and iron begins and proceeds the faster the higher the temperature is raised. The steel, on cooling, remains in the same condition as when hot; and if we discontinue heating at the suitable time we

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can vary the proportion between the carbide, on the one hand, and iron and carbon, on the other, and thus obtain, within certain limits, any degree of hardness.

P. I do not quite understand. You told me that the carbide was formed by heat, and then you say that it decomposes on raising the temperature. How do you reconcile these contrary facts?

M. It is merely a contradiction in terms, for the tempering heat is much less than that required to produce the carbide. And although, during the former process, the greater portion of the carbide decomposes, still it does so little by little and not all at once.

P. Ah! I think I understand now. Why is steel so much more expensive than other kinds of iron?

M. Because, for good steel we have to use only the purest iron, and this is naturally dearer than the ordinary, cruder variety which generally contains silicon and a little sulphur. Both these elements make steel brittle, but do little harm to cast iron. Well, I have now said enough about the metal itself. Later on, when we have studied its compounds, I shall show you how we prepare the different varieties of iron from the rough ores. Let us examine the solution which we prepared with the hydrochloric acid. What does it look like and what is in it?

P. It is slightly greenish. It contains a chlorine compound of iron.

M. Quite right. A salt of the divalent ferrous ion, $Fe^{\cdot\cdot}$, has been formed. Write the chemical equation.

P. $Fe+2HCl=FeCl_2+H_2$. Is that right?

M. Yes. The ferrous ion (so called from *ferrum*, the Latin for iron) has a delicate green colour and an inky taste, i.e., ink contains it and tastes of it.

P. Is it poisonous?

M. No. Iron is found in all living organisms. It is present in the green leaves of plants and the blood of animals. If

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I decompose the solution with caustic potash a greenish precipitate of ferrous hydroxide is formed. This quickly darkens on shaking. On exposure to the air for some time it turns brown.

P. Why is that?

M. Ferrous hydrate absorbs atmospheric oxygen and changes into a compound of a different colour. If we dissolve iron in sulphuric instead of hydrochloric acid, we obtain its best known salt, ferrous sulphate or *green vitriol* (*copperas*). This is a greenish substance which contains water of crystallization and has the formula $FeSO_4+7H_2O$.

P. What does the word "vitriol" mean?

M. A sulphate of a heavy metal. Before we knew much about their chemical compositions, we used to class together certain salts of similar appearance and call them vitriols. That is how the name came to be retained and extended to other sulphates.

P. But do we not also call sulphuric acid vitriol?

M. It used to be spoken of as *oil of vitriol;* since it is of an oily nature and was formerly prepared from green vitriol, which decomposes under strong heat into sulphur trioxide and iron oxide. In those days this was the only method of preparation, as we then knew nothing about producing sulphuric acid by burning sulphur and oxidizing the sulphur dioxide. Its manufacture was carried on at Nordhausen, in the Harz mountains, and therefore you sometimes hear the name *Nordhausen sulphuric acid.* The green vitriol used for this purpose is obtained in large quantities by allowing a mineral, iron sulphide, which is very prevalent there, to oxidize by simple exposure to the air. Oxygen is absorbed and ferrous sulphate is formed:

$$FeS+2O_2=FeSO_4.$$

Green vitriol is useful in many ways, for example, in the colour industry and the manufacture of ink. In the latter process

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they mix the iron salt with the extract from gall-nuts, which contain an organic substance, tannic acid. These two constituents unite and form a black compound. The bark and wood of oak contain tannic acid. You will often detect a violet-black colour where an iron nail has been driven into a damp oaken board.

P. But ink often gives a pale impression, which only darkens after an interval.

M. That is because the ferrous salt present at first has become more highly oxidized by taking up oxygen from the air, and has thus changed into a compound of a much darker colour.—Of the other salts of iron, the carbonate, $FeCO_3$, is the only one worth mentioning. It is sometimes found in nature in great quantities under the names of *siderite* or *spathic iron ore.* It resembles calc-spar in its crystalline form, but is of a dark or greenish-grey colour. Metallic iron is obtained from it by smelting.

32. IRON II.

P. On going over yesterday's lesson to myself I was rather puzzled about your allusions to the more highly oxidized compounds of iron. What are they?

M. Well, you have already met with some instances of the same kind. For example, sulphur forms sulphur dioxide and sulphur trioxide, which correspond to sulphurous acid and sulphuric acid. Write their formulæ.

P. SO_2 and SO_3 correspond to H_2SO_3 and H_2SO_4. Yes. Here we have an increase of one combining weight of oxygen.

M. And under suitable conditions this addition is brought about by the action of atmospheric oxygen. Iron acts analogously. As I showed you, it has one hydroxide, $Fe(OH)_2$, which corresponds to the divalent ferrous ion and has the anhydride FeO, resembling calcium oxide, CaO. (P. 231.) This FeO compound we call ferrous oxide (sometimes prot-

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oxide of iron), according to the rule I gave you on p. 7. It is not very easily prepared, but can be obtained as a dark powder, which on exposure to the air immediately combines with more oxygen and forms a higher oxide with the name ferric oxide (sometimes sesquioxide of iron), and the formula Fe_2O_3. This will remind you of Al_2O_3, the formula of aluminium oxide, to which compound ferric oxide bears a great similarity. In fact, it is just because of this resemblance that we chose the combining weight of aluminium so that its oxide could be represented by the formula Al_2O_3. Here is a sample of natural ferric oxide, called *specular iron ore.*

P. These are beautiful, shining crystals. They look something like metallic iron.

M. They are similar in form to corundum, the crystalline oxide of aluminium. (P. 253.) If we pulverize them they lose their bluish-black glitter and turn dark red, like artificially prepared ferric oxide. The colour of the latter varies, according to the conditions under which it is prepared, from fairly bright red to dark violet.

P. On what do these conditions depend?

M. The temperature. As the heat is raised the granules of oxide become larger and approximate more nearly in colour to the crystalline specular ore. We use the bright-red variety as a pigment under the name of *rouge;* the darker qualities are known as *colcothar* (*caput mortuum*).

P. That last name means death's-head. How did this substance get such a horrible name?

M. I told you that we used to obtain sulphuric acid from green vitriol by distillation when this ferric oxide was left behind as a residue. The process was compared to death; they said that of the body the skull alone remained; and the sulphuric acid, as it vaporized away, was likened to the passage of the spirit as it leaves the worthless clay which has confined and would still retain it.

P. How did they get this curious idea?

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M. Whenever there is a strange thing which we cannot understand we try to express its meaning by some familiar resemblance. Think of the anecdote of the horse in the locomotive! The less we know of a subject the more do we draw upon our imagination to afford comparisons which are creatures of our fancy and have little basis on fact. In the middle ages, when such phenomena as these were still looked upon as signs and wonders, man considered that the universe was focussed in himself, and that it had been made not only for his sole benefit, but also after his own image. Thus they always sought to interpret the workings of nature according to human ideas and in the language of everyday incidents; and man himself they called a microcosm, or world in miniature.

P. What nonsense that was!

M. It is only because we belong to the twentieth century that it strikes us as absurd. Many traces of those early beliefs still cling not only to our conversation, but even to our ways of thinking.—Ferric oxide also appears in nature in combination with ferrous oxide,

$$Fe_2O_3 + FeO = Fe_3O_4,$$

as *mangetic iron ore* (*loadstone*). This is a most important and valuable mineral.

P. How did it obtain its name?

M. Because it is frequently found to have magnetic properties. The first compasses ever known contained "natural" magnets made of this oxide, which can magnetize not only iron, but also all its compounds, though generally to a much smaller extent. In many cases magnetic iron possesses the same property.

P. What does "magnetism" actually mean?

M. It is an energy, just as there is electric energy. Do you know any effect produced by magnetic force?

P. It attracts iron.

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M. Yes. It is made to unite with the magnet, and it is then in a position to perform work like the other energies. We make use of this work in driving dynamos, since electric, magnetic, and mechanical power are easily convertible one into the other.

P. I tried to see how many pieces of steel I could magnetize with my magnet. I have managed to make all the nibs in my desk magnetic, and I seem to get an unlimited amount of this energy from nothing.

M. Not from nothing. For you had to do work to remove the magnet from the magnetized nibs, and these can, in their turn, communicate the energy thus imparted to them.

P. So each of these nibs can magnetize as many others as we wish?

M. Certainly. But never without the expenditure of fresh work. You do no more than increase the quantity of magnetic energy at the cost of another form of energy. However, this is a somewhat difficult subject and you must wait for a clearer insight into it until you take up the study of physics. Let us return to the ferric oxide. It, again, is the anhydride of ferric hydroxide, $Fe(OH)_3$, which likewise is found in nature under the name of *brown iron ore.* When powdered it has a yellow, varying to brown, appearance (not red like the oxide) and imparts a yellow colour to substances mixed with it. Thus a mixture of ferric hydrate with clay is used as a pigment and is known as *ochre.*

P. I have in my paint-box, besides yellow ochre, burnt ochre, which is red.

M. The latter is prepared by heating the yellow variety, which then loses water and becomes red by changing into the oxide. For the same reason, much of our pottery, our bricks and so forth, are yellow in the unfinished state, but turn red on being fired. The equation is:

$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O.$$

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P. I noticed, the other day, that a bluish-grey clay went red on being burnt.

M. It must have contained iron in a partially oxidized condition, due probably to the presence of organic matter. On heating complete oxidation ensued. The compounds intermediate between ferrous and ferric oxide are dark in colour. They are produced when we heat iron, i.e., make it burn in the air.

P. Perhaps that black powder which was formed when we ignited iron filings on the balance (I. p. 69) consisted of partially oxidized iron?

M. Quite right. Its composition nearly approximated to that of the magnetic oxide. A certain amount of the same compound is produced when iron is heated in the smithy. It falls to pieces under the hammer because it is brittle; it is, therefore, called *hammer-scale* (*clinker*). Just examine some next time you visit the blacksmith.

P. Did you not say that rust is also an oxide of iron?

M. It is simply ferric hydrate, $Fe(OH)_3$. It is formed by the simultaneous effect of the air and moisture. But far from protecting the metal beneath it, as aluminium hydroxide does, it facilitates further oxidation. This is evidenced by the fact that a rust-stain does not spread itself uniformly over the surface, but works downwards. The iron is thus weakened or perforated at the place attacked, a result that is often attended with considerable danger in the case of boilers, bridges, etc.

P. Is there any method of protecting the iron?

M. Yes; by providing it with a coating impervious to moisture and air. This is done in many different ways; by covering the surface with a layer of other metals (such as tin, zinc, nickel, or lead) in the form of paint, or by putting on a compact jacket of iron oxide. But whenever a breach appears in the protecting coat the rust is very apt to enter

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through it. Iron does not rust in dry air, but, on the other hand, does so rapidly in contact with salt water.

P. Is that because of the sodium chloride?

M. Yes. Some complicated chemical reactions ensue, but to explain them would lead us too far afield.—I pour hydrochloric acid over some of the yellow hydroxide and warm: we obtain a dark yellow solution which contains a salt, ferric chloride. Write the equation.

P. $Fe(OH_3)+3HCl=FeCl_3+3H_2O$.

M. Right. You see, we have here not a divalent, but a trivalent iron ion, which we distinguish as the ferric ion, $Fe^{\cdots}$, from the divalent ferrous ion, $Fe^{\cdot\cdot}$.

P. But as both are simply iron how can we make any distinction?

M. The difference is the same as that between graphite and diamond, or between white and red phosphorus. We can look upon them as allotropic forms of the iron ion, for they contain different amounts of energy. The essential point is that they vary in valency, and therefore in their chemical behaviour; for the salts of the divalent iron resemble those of magnesium, while the trivalent iron compounds are like those of aluminium, as you will soon see.

P. Yes; you have already told me that ferric oxide has the same crystalline form as aluminium oxide.

M. Such an analogy can be traced between many others of their corresponding compounds. Here is some solid ferric chloride. It has a green, metallic sheen, such as some beetles have. It is prepared by heating iron in a current of chlorine.

P. Could we not obtain it by simply evaporating the solution of ferric oxide in hydrochloric acid?

M. No; that would not act. We would obtain this yellowish-brown salt, which is ferric chloride in combination with 6 molecules of water of crystallization. If we try to drive

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away these last traces of water, hydrogen chloride is given off and ferric hydroxide remains behind:

$$FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl.$$

This reaction is just the reverse of that which occurred when we dissolved the ferric hydrate in the acid.

P. Then how was this counter effect possible?

M. Ferric hydroxide is a weak base, even feebler than aluminium hydroxide; and so a solution of ferric chloride in water is partially broken up into free acid and base; and as we expel the former by evaporation a fresh quantity is always being formed to take its place, until finally all the salt is decomposed. This dissociation is especially noticcable on applying heat. Just watch. I dilute a solution of ferric chloride until the colour almost disappears, divide it in equal portions in two test-tubes, and bring one nearly to the boiling-point.

P. The liquid has turned quite reddish-brown.

M. That is because the ferric hydrate has separated from the salt. However, it is not precipitated, but, like the silicic acid (p. 198), remains dissolved in a colloidal form. I now cool the test-tube by immersing it in water. The colour still remains dark, because colloidal ferric hydrate unites but slowly with hydrochloric acid. If you keep the two portions for a few days you will see that the colour of the once warm solution keeps diminishing until eventually both test-tubes look alike.

P. I shall watch carefully and see if this happens!

M. If I cautiously mix caustic potash, drop by drop, with a fairly concentrated ferric chloride solution I obtain a dark, reddish-brown liquid, produced by the colloidal ferric hydrate thus formed dissolving in the still undecomposed ferric chloride. By taking suitable precautions we can prepare solutions containing almost nothing but this colloidal hydroxide of iron. They are dark reddish-brown in appearance,

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and are sold by apothecaries for medicinal purposes under the name of *dialysed iron.*—Here is still another salt of iron It is called *iron alum.*

P. What pretty crystals! They somewhat resemble those of potash alum, but these are brownish-violet.

M. The formula of this substance is $FeK(SO_4)_2 \cdot 12H_2O$; it is very similar to that of alum (p. 257), only we here have Fe instead of Al. Both compounds correspond in their crystalline form. This is a striking instance of how like iron is to aluminium. I dissolve some iron alum in water.

P. The liquor looks brownish, but not nearly so yellow as the ferric chloride solution. Then what really is the colour of the ferric ion? I thought it was yellow.

M. If coloured at all it is slightly yellow. The brown tinge of this solution is caused by the presence of a little colloidal hydrate. If I remove this by adding some nitric acid the liquid becomes almost colourless.

P. So I see. Then why is the ferric chloride solution yellow?

M. Because that is the colour of the undissociated salt.—Let us now leave these compounds, and I will tell you something about the connection between the ferrous and ferric salts. Write down the formulæ of ferrous and ferric chloride, and show me how you would convert one into the other.

P. $FeCl_2$ and $FeCl_3$. In order to change the first into the second we must add chlorine.

M. Right. I add some chlorine water to our ferrous chloride solution, and it immediately becomes yellow. Of course, instead of chlorine we could have taken hydrochloric acid and decomposed it with some oxidizing agent. Make two experiments afterwards for yourself, first with potassium chlorate, and then with bleaching-powder. Nitric acid also has the same effect.—The part played by the above reagents enables us to look upon the change of a ferrous into a ferric salt as an oxidation process. Conversely, the counter

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reaction can be carried through by means of reducing agents. How would you remove chlorine from ferric chloride?

P. By using some substance, such as one of the other metals, which would unite with chlorine.

M. Quite right. I shake up the yellow solution with magnesium powder, and filter.

P. The filtrate is colourless.

M. Zinc has the same, but a slower effect. Write the equation; and remember in what proportions chlorine and magnesium combine.

P. Two of the former unite with one magnesium, and one ferric chloride gives up one chlorine; so we have

$$2FeCl_3 + Mg = 2FeCl_2 + MgCl_2.$$

Is that correct?

M. Yes. Just take iron instead of magnesium.

P. Hm! How shall I manage that?

$$2FeCl_3 + Fe = 2FeCl_2 + FeCl_2.$$

M. Can you not write that more simply?

P. I suppose I ought to add the $FeCl_2$ together? Then I have,

$$2FeCl_3 + Fe = 3FeCl_2.$$

The product consists of nothing but ferrous chloride.

M. Right. This shows you that we can convert a ferric into the corresponding ferrous salt without introducing any foreign substance.—But we must not forget the sulphur compounds of iron. You met with one of these when we were dealing with hydrogen sulphide.

P. Hydrogen sulphide? Ah! yes; I remember. For its preparation we used a black substance which had the formula FeS.

M. Yes. It was the ferrous sulphur compound, and, therefore, it gave ferrous chloride and hydrogen sulphide on

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treatment with hydrochloric acid. We have no natural ferric sulphur compound to correspond with $FeCl_3$, but, on the other hand, large quantities of the compound FeS_2 are found in nature under the name of *iron pyrites*. This substance is somewhat out of the common since, as you will see later on, most of the other heavy metals form sulphur combinations exactly analogous in composition to their oxygen compounds. Here are some pieces of pyrites. Describe them.

P. They have a metallic appearance, something like brass, only perhaps rather greener. They are, for the most part, in small crystalline cubes.

M. Quite right. I place some in a narrow test-tube and heat strongly. What do you see?

P. Something is depositing on the upper portion of the glass. I should say it was sulphur. Let me smell! Yes. There is sulphur dioxide there.

M. Correct. Pyrites loses half its sulphur and changes into ferrous sulphide when the air is excluded; but if roasted and exposed to the atmosphere all the sulphur is burnt and the iron is left as ferric oxide. This is how the sulphur dioxide used in the manufacture of sulphuric acid (p. 144) is obtained. Ferrous sulphide when left in moist air is converted into ferrous sulphate (p. 267).—Iron and sulphur combine very readily. Just mix some iron filings and powdered sulphur in the proportion of their combining weights, 56:32, and heat one portion in a dry test-tube.

P. Oh! The whole mass has got red-hot.

M. Ferrous sulphide has been formed. Moisten another portion with water and set it aside in a small jar; we shall examine it to-morrow.—Let me remind you that if I pour some hydrogen sulphide into a solution of a ferrous salt, I obtain no precipitate (p. 156); but, as I showed you before, on the addition of caustic potash the greenish-black ferrous sulphide is thrown down.

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33. IRON III.

P. I have just been examining the mixture in the jar. It has turned into some black substance. Is it ferrous sulphide?

M. You can easily test if it is. What are some of its properties?

P. It gives off hydrogen sulphide with hydrochloric acid. May I try if this does? Ugh! There is no mistaking that smell!

M. So you see that these two elements can unite even at the ordinary temperature; of course, only slowly, but still fast enough to enable us to detect the result. I let you make this experiment to give you an example of a slow reaction.

P. But, in this case, where has the heat gone? I know that some must have been produced in the reaction from the way in which the mixture in my test-tube got red-hot. For, if I understood you correctly (p. 182), the same amount of energy is given out whether the combination goes fast or slow.

M. Very good. You are quite correct. The quantity of heat is the same in both cases, but in the last instance it has been dissipated by conduction. If we pack the cold mixture well together so that it retains the heat, the whole mass will become red-hot. But, of course, it takes a good long time for so much energy as will effect this to accumulate.

P. Oh! How I would like to make that experiment!

M. Well, if you put a few pounds of the damp mixture in a jar and bury it in the ground you will soon have quite a fine earthquake. But you must choose a spot where it will cause no damage or danger from fire.—But I must tell you how we prepare iron from its ores. The process is not easy, because the melting-point of the metal is high; and that is why the ancients were familiar with gold, silver, and copper

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long before iron was known. Only the oxygen compounds are employed in the preparation.

P. Why do they not take pyrites since it is so abundant?

M. Because the presence of sulphur has such a harmful effect on the properties of iron that we always avoid ores which contain it. Alternate layers of the ore, charcoal, and

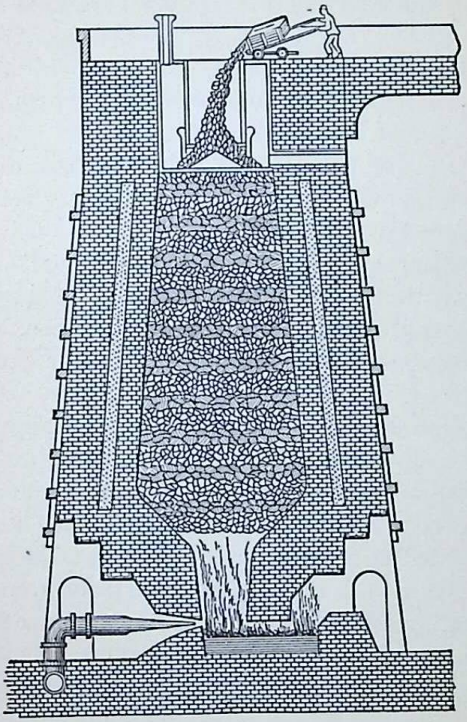

FIG. 30.

a so-called fluxive material (which serves to form a fusible slag with the impurities in the iron) are thrown into a large oven, called a blast-furnace, at the bottom of which a blast of heated air is admitted. Fig. 30 shows you the furnace in operation. The molten iron collects at the bottom, along

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with the liquid slag, and is drawn off from time to time through a hole.

P. What is the chemistry of this manufacture?

M. It is pretty complicated. The charcoal burns in the lower part of the furnace to carbon monoxide, which is then driven upwards, and on its way reduces the ferric oxide to iron, according to the equation

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

This occurs fairly high up, because only slight heat is necessary.

P. Then is the whole process finished there?

M. By no means. At this low temperature the metal is of a spongy nature and not in a coherent mass. As the mixture of iron and charcoal passes down into the warmer parts of the furnace a combination ensues and a much more fusible mixture of iron carbide and excess of iron is formed. This melts as it penetrates into the hotest part, and collects at the bottom, as I described to you.

P. Is it then cast iron?

M. Yes; or, as it is sometimes called, *pig iron.* What must we do to convert it into wrought iron and steel?

P. These contain less carbon; so this must be removed.

M. Yes. We burn it away. The cast iron is heated and so manipulated that every part is exposed to the action of the air. Nearly all the carbon escapes as an oxide, and the residual metal is left with almost none. In this way we can prepare either steel or wrought iron.

P. That is to say the former is formed first, and then the latter.

M. Yes; but only the purest of ores are suitable for the direct preparation of steel. The usual plan is to make wrought iron first, thus getting rid of any impurities, and then convert this into steel.

P. By again introducing carbon. Do we melt it in?

M. No; that is unnecessary. If we pack the metal in

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powdered charcoal and heat strongly for a considerable time, the iron absorbs an amount proportional to the duration of the heating process, which is, therefore, stopped after the proper interval. However, most of the carbon is then situated near the surface and, in order to make the steel uniform, we must either remelt or, as is often done, recast it. This is known as the *cementation process*, and the product, on account of its appearance, is called *blister-steel*. Another method is to fuse wrought iron with the quantity of cast iron necessary to produce a mixture of the constituency of steel; but for this manufacture the materials at our disposal must be pure.—Well, that will do for the chemistry of the preparation of iron. I will now show you some other, more complicated compounds peculiar to this metal. Do you remember cyanogen and hydrocyanic acid?

P. Yes; the latter is also called prussic acid.

M. Quite right. You will now find how it gets its name. I add potassium cyanide to a solution of a ferrous salt; at first a precipitate is formed; but this, on a further addition of the cyanide, dissolves and produces a pale-yellow solution which does not give the iron reaction. I can add any amount of caustic potash without obtaining a precipitate of ferrous hydrate. And even if I add hydrogen sulphide to the basic solution no ferrous sulphide is thrown down. (P. 156.)

P. Then where has the iron gone?

M. It is there, but not as the ferrous ion; for this has entered into a very stable combination with the cyanogen, according to the following equation:

$$FeSO_4 + 6KCN = K_4Fe(CN)_6 + K_2SO_4;$$

or, if I take into consideration only those ions of interest to us,

$$Fe^{\cdot\cdot} + 6CN' = Fe(CN)_6''''';$$

you see the ferrous ion unites with 6 cyanogen ions and forms a tetravalent anion. The potassium salt of this

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anion is present in the solution and is called *yellow prussiate of potash.* This was first obtained by heating dried blood, and extracting it from the residue with water. The constituents of the blood, namely, the carbon and nitrogen of the organic matter and the potassium and iron in the corpuscles, unite together to form this compound; but the reaction is too complicated to be represented by an equation. Look at the formula of this salt. What are its ions?

P. Four potassium are the cathions and $Fe(CN)''''_6$ is the anion. What is the latter called?

M. It is the ferrocyanogen ion and the salt itself is potassium ferrocyanide. So strongly are the properties of iron and cyanogen modified in the ferrocyanogen ion that it gives the reactions of neither. More especially, it is not poisonous though both its constituents are. Such ions, which are combinations of other simpler ones, we designate as complex. If an ion, which we expect should be present, does not declare itself by the usual tests, then we have every reason to assume that it has been changed into a more complex ion; and this, of course, will have its own reactions peculiar to itself. I add some potassium ferrocyanide to an extremely dilute solution of ferric chloride—

P. What a magnificent blue colour!

M. This effect was first discovered by Dippel, a chemist in Berlin, in the eighteenth century, and the substance thus produced was called *Berlin* or *Prussian blue.* (This used to be the source for the preparation of prussic acid, hence the name.) It was afterwards spoken of as *Paris blue,* but this title is superfluous and should be discarded. Just think out the reaction for yourself; it is a simple case of salt formation.

P. Well, then, the ferric ion must have combined with the ferrocyanogen ion. The former is trivalent, the latter is tetravalent, so I must unite four iron with three ferrocyanogen. Is that right? Yes; then the formula is

$$Fe_4(Fe(CN)_6)_3.$$

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M. I add caustic potash to the blue liquid. The colour disappears and, as you see, some brown ferric hydrate is precipitated. The ferric salt has been decomposed by the base and potassium ferrocyanide has been reformed. Write the equation.

P. I shall require twelve potassium hydrate for the four trivalent iron, so

$$Fe_4(Fe(CN)_6)_3 + 12KOH = 4Fe(OH)_3 + 3K_4Fe(CN)_6.$$

M. Correct. You manage these calculations admirably.

P. I must confess that I always have a risky feeling about equations, but I take courage from the thought that they must come right if I only keep strictly to the rules.

M. In every case there is at least one possible reaction, and experiment must decide whether that particular one takes place under the given conditions. Thus you see ferrocyanogen is a compound ion like the sulphate or the phosphate ion, but differs from these in containing a metal and in being tetravalent. Of course, it can form an acid. This is obtained by decomposing a concentrated solution of the potassium salt with strong hydrochloric acid, thus:

$$K_4Fe(CN)_6 + 4HCl = H_4Fe(CN)_6 + 4KCl.$$

The acid separates out in bluish-white crystals. It is, however, very unstable and we shall not bother ourselves further with it. Let me rather show you some of the reactions of potassium ferrocyanide. If, instead of a ferric, I take a ferrous salt, such as green vitriol, I also obtain a precipitate—

P. But this one is bright blue!

M. It is white when quite pure; the smallest trace of oxygen turns it blue. You will observe that it is darker near the top, where it is in contact with the air. This is the ferrous salt of the ferrocyanogen ion. What is its composition?

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P The ferrocyanogen ion is tetravalent, the ferrous ion divalent; therefore I need to take just two of the latter: $Fe_2Fe(CN)_6$.

M. Good. So potassium ferrocyanide serves as a test for both ferrous and ferric compounds; it gives with the former a white or bright blue, with the latter a dark-blue precipitate.

P. But supposing we have a mixture of both salts?

M. Then we can only detect the ferric, because only a small quantity of this is sufficient to give a dark-blue appearance to the precipitate.—I now add some chlorine water to a solution of potassium ferrocyanide.

P. It turns a much darker yellow.

M. Another compound is formed according to the equation

$$K_4Fe(CN)_6 + Cl = K_3Fe(CN)_6 + KCl;$$

or, if I simply write the ions which concern us,

$$Fe(CN)_6'''' + Cl = Fe(CN)_6''' + Cl'.$$

Our previous tetravalent anion, $Fe(CN)_6''''$, has now changed into a trivalent compound by passing on one of its valencies to the chlorine which has, by this process, been converted into the chlorine ion. $Fe(CN)_6'''$ is called the ferricyanogen ion; and this dark brownish-red substance, almost the colour of a garnet, is its potassium salt, potassium ferricyanide. It is sometimes called *red prussiate of potash*. It forms a deep-yellow solution with water.

P. This new anion has exactly the same composition as the ferrocyanogen ion.

M. Certainly. They only differ in the proportions in which they combine with cathions. Their names indicate their nature, namely, that the ferricyanogen is an oxidation product of the ferrocyanogen ion; just as the ferric is of

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the ferrous ion. Again, the ferricyanogen can be converted into the ferrocyanogen ion by a reducing agent.

P. But how does it happen that with iron the valency increases on oxidation and with ferrocyanogen it diminishes?

M. That is because in the one case we are dealing with cathions, in the other with anions. The valency corresponds to the amount of electricity contained in the ions; their oxidation means an increase in their quantity of positive electricity. So if we add, by oxidation, one positive to the four negative units of the ferrocyanogen ion three negative units remain over.

P. I do not yet understand.

M. You remember that the metallic ion is produced from the metal at the anode where the positive electricity enters the electrolyte. (P. 96.) Well, an oxidizing agent exerts just the same effect; for example, chlorine water or nitric acid, if allowed to act on a metal, converts it into its ion. Therefore a charge of positive electricity is equivalent to an oxidation effect. But if we oxidize an anion, say the iodine ion, it changes into its corresponding element, in the present case free iodine, as this effect is equivalent to the loss of a charge of negative electricity, because a positive cancels a negative.

P. Then the simplest method is to look on the ions as substances laden with electricity; the cathions with positive, the anions with negative charges. (P. 96.)

M. Quite right. And, indeed, a divalent contains double the charge of a monovalent ion, while the trivalent and tetravalent ions contain three and four times that amount.

P. Then how is it that salt solutions, which contain these electrically charged ions, produce no sparks and show no forces of attraction or other properties usual to electrified objects? At least I have never noticed anything of the kind.

M. Because in every solution the positive and negative ions are equivalent to each other; so the total sum of all the

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amounts of electricity comes to zero and is incapable of exerting any effect. We cannot prepare a solution so that it will contain only chlorine ions or only potassium ions. If we could we would obtain a liquid electrified to an excessively high degree.

P. Then it is only from circumstantial evidence that we say that the individual ions are electrically charged.

M. You are quite right. All we know is that when a metal changes into its ion a certain quantity of positive electricity passes, simultaneously with the metal, into the solution, and in so doing converts the metal into its ion. And that if we, on the other hand, remove this positive electricity, the metallic ion is converted back again into the corresponding amount of metal. These facts can be represented most simply by representing the electricity as being contained by the ions. So you will not be wrong if you look on them as being electrically charged, even though no effective electric energy is apparent.—Now let me show you some reactions with the ferricyanogen ion. If I add a solution of the potassium salt to a ferrous compound, I obtain a dark-blue precipitate which looks like the one produced by a ferrocyanide with a ferric salt.

P. Are they the same?

M. No. They differ in composition. This one, which contains the divalent ferrous ion and the trivalent ferricyanogen ion, has the formula $Fe_3(Fe(CN)_6)_2$, and is known as *Turnbull's blue.* It contains 5 iron to 12 cyanogen, while in the former compound there are 7 to 18. This one contains 15, and the former only 14 iron to 36 cyanogen. To be sure the difference is not great; both these salts resemble each other in appearance and behaviour towards other substances. But if I add my ferricyanide solution to a ferric salt, not a trace of precipitate is formed; the solution only turns a little darker.

P. How is that?

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M. Just because the ferric salt of ferricyanogen is soluble. So after this we shall be able to detect small quantities of a ferrous salt in the presence of a great deal of a ferric salt; for if even a little of the former is present, a blue precipitate will be formed. Conversely, we can recognize with the ferrocyanogen slight traces of a ferric salt in the presence of a ferrous compound. In conclusion, let me remind you that the two prussiates of potassium provide us with tests for detecting iron *where iron is not present as such;* that is to say it is there, but not as its ion. We are apt to forget that the test for a metal is not always identical with that for its ion.

34. MANGANESE.

P. You told me that the chemistry of the metals was comparatively simple, but my last lesson was quite complicated enough. I think I understood all you said, though I feel a little shaky on the subject.

M. You will see that many of the reactions connected with iron have their counterpart with other metals; this will help you to get familiar with these new ideas in the same way that your detailed study of hydrochloric acid was of use in enabling you to understand the properties of other acids. Indeed, manganese, our subject for to-day, resembles iron in many respects. Here is some. It has a distinctly reddish lustre, but is rather like iron, and oxidizes more easily in damp air, forming a dark-brown rust. Acids, also, dissolve it faster; the solutions are a pale rose colour.

P. Is it put to the same uses as iron?

M. No. It is scarcely ever employed in the metallic condition, except to mix or alloy with iron in the preparation of a steel, which is of advantage for certain special purposes.

P. You said "alloy"; what is that?

M. A composition of two or more metals is called an *alloy.*

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It generally resembles its individual constituents in appearance, and is, in many cases, merely a mechanical mixture.—The rose coloured solutions, obtained by dissolving metallic manganese in acids, contain the salt of the divalent manganese ion, $Mn^{\cdot\cdot}$, which is very similar to the magnesium ion. Write the reaction with sulphuric acid.

P. $Mn+H_2SO_4=MnSO_4+H_2$.

M. Right. Here is some of this manganese sulphate. It is also pale red. If I add the hydrate of potassium or of sodium to the solution, I obtain a precipitate of the hydroxide, $Mn(OH)_2$, which likewise is reddish in colour.

P. But it is rather brown toward the top.

M. Because it behaves just like the hydroxide of the divalent iron; it absorbs oxygen from the air and is converted into a dark brown compound. However, the higher hydrate thus formed is not a base, for it is incapable of forming salts. If we try to obtain salts of the trivalent manganese by other methods they decompose into the free acid and this brown hydrate, $Mn(OH)_3$, which is precipitated.

P. Then I won't be bothered with any trivalent varieties to-day?

M. No; but this element has plenty of other compounds which will keep you occupied. You have already had to do with one, brown manganese dioxide, MnO_2. What do you know about it?

P. It is used in the preparation of chlorine; its oxygen combines with the hydrogen in the hydrogen chloride. (P. 5.)

M. Yes. We shall now consider this reaction in more detail. I have here a little artificially prepared manganese dioxide in the form of a very fine powder. I pour concentrated hydrochloric acid over it.

P. It appears to form a dark greenish-brown solution.

M. Yes; it contains manganese tetrachloride,

$$MnO_2+4HCl=MnCl_4+2H_2O.$$

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(Tetra is the Greek for four.) On warming, this compound decomposes into the dichloride and chlorine,

$$MnCl_4 = MnCl_2 + Cl_2.$$

Here you see one way of detecting manganese dichloride, it has the rose-red colour of the other salts of the divalent manganese ion; and the liquid in my test-tube, now that the chlorine has been driven off, shows this same tint.

P. Then, to what class of substances does manganese dioxide really belong? It seems to be neither an acid, a base, nor a salt.

M. It is what is known as an indifferent substance. Carbon monoxide is another. However, manganese dioxide behaves, in many respects, as the anhydride of a weak, dibasic acid, H_2MnO_3; but its compounds (which may be looked on as its salts) are few and by no means regular in composition.

P. Thus, so far, we have three varieties of manganese compounds.

M. Yes; and there are still two more. I melt on a piece of platinum foil a mixture of the carbonates of sodium and potassium,—for the salts by themselves would not fuse so easily.

P. Why not?

M. Because the melting-point of any substance is always lowered when we add to it some other material which forms a mixture or solution with it in the liquid state. Now I add a trace of some manganese compound and continue to fuse for some seconds.

P. The liquid appears to be glowing more brightly.

M. That is because it has become less transparent. (P. 248.) I let the mass cool—

P. It has turned quite dark green, nearly black.

M. Yes. A new manganese compound has been produced. Here is a more considerable quantity of this product, formed

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by heating manganese dioxide with potassium carbonate. It is so dark a green that it looks black; but if I dissolve a little in water I obtain a beautiful dark-green solution.

P. And what is it?

M. It is the potassium salt of a new anion, which is produced by the addition of oxygen to manganese. It is called potassium manganate, and has the formula K_2MnO_4, thus resembling potassium sulphate, K_2SO_4. Both these salts, indeed, have the same crystalline shape, and are, therefore, called isomorphous, or of the same form. You have already seen an instance of a similar resemblance in the case of alum and iron alum. (P. 275.) The new anion, MnO_4, is called the manganate ion.

P. But, look! What has happened to the solution? It is no longer green, but blue or violet.

M. Were I to let it stand for some time longer it would eventually turn to a reddish purple. I can effect this change at once by adding a little chlorine water.

P. What a beautiful colour! Has a new salt been formed? What has become of the previous one?

M. What surprised you was also a matter of astonishment to the early chemists, and they gave the green salt the mineralogical name of *chameleon*, because it changes its colour after the fashion of that animal. The process is not difficult to understand. At first we had the ions $2K^{\cdot}$ and MnO_4'' in the solution! When I added chlorine water a reaction ensued similar to that which occurs on pouring chlorine water into a yellow solution of potassium ferrocyanide; a negative charge passes from the manganate ion, MnO_4'', into the chlorine, and a new monovalent ion, MnO_4', is produced. This we call the permanganate ion. Write the equation.

P. $MnO_4'' + Cl = MnO_4' + Cl'$.

M. Quite right. As you see, we again have two ions exactly the same in chemical composition, but differing in

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their valency and electric energy (p. 284), and, even more so, in their properties.

P. Ah! I am now much clearer on this subject than I was. But there is one thing I do not understand: why did the green solution become red of its own accord? Was it oxidized by the atmospheric oxygen?

M. No. The change was brought about by the carbonic acid in the air. If I add some acid to a freshly prepared green solution the red colour appears immediately.

P. So I see; but is it not rather more of a brownish red?

M. Quite right; it is; and because of the following facts: in order for the manganate to turn into the permanganate ion there must be an oxidation. This I first carried out by means of chlorine, and it provided you with another example of how the effect thus obtained was equivalent to a decrease of the negative charge. (P. 285.) If I simply add an acid then one portion of the manganate ion serves to oxidize the other portion to the permanganate ion, and is reduced, in so doing, to manganese dioxide. The latter is insoluble in the acid, and separates out as a fine brown cloud which gives to the whole solution a slightly browner appearance. The following is the equation if we use sulphuric acid:

$$3K_2MnO_4 + 2H_2SO_4 = 2KMnO_4 + MnO_2 + 2K_2SO_4 + 2H_2O.$$

But since any other acid would have the same effect, let us simply write the ions which illustrate the change:

$$3MnO_4'' + 4H^{\cdot} = 2MnO_4' + MnO_2 + 2H_2O.$$

You see, hydrogen ions enter into the reaction, and that explains why the process only goes in an acid solution.

P. Please tell me how must we calculate the number of strokes and dots in an ion equation?

M. You know that a cathion has as many dots as it has valencies and charges of positive electricity, just as each

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stroke corresponds to a negative charge. When you write an equation, showing all the ions which are present in a solution, you must have as many strokes as dots, both on the right side and on the left, because the sum of all the charges must come to zero; otherwise the solution would behave as a body highly charged with electricity. (P. 285.) But if we write an abbreviated equation, from which the ions remaining unchanged are left out, then all we have to beware of is to have the same excess of dots or strokes on both sides. Thus, in the last equation we have on the left $3 \times 2 = 6$ strokes and 4 dots, in other words, an excess of two strokes; and on the right we have two strokes and no dots.

P. Thank you. I think I understand now.

M. Well, then, let us return to our permanganate ion. Its best-known compound is the potassium salt. Here is some.

P. It has a metallic glitter.

M. That is because of its strong colour. If I just strew some small particles over the surface of a large quantity of water in a beaker, you see how dark-red streaks form, and when I shake, the whole liquid turns red.—Potassium permanganate is a powerful oxidizing agent. For example, when I add a little sulphurous acid to my solution it immediately loses its colour, because the permanganate ion changes into the almost colourless divalent manganese ion. A somewhat concentrated solution of the salt makes the skin and many other organic substances brown, since it gives up oxygen and is reduced to manganese dioxide, which adheres in the form of an insoluble precipitate. It may, therefore, be used to disinfect and to bleach. The brown dioxide deposit can be removed with sulphur dioxide. Write the equation.

P. As I do not know what actually happens I must make a guess:

$$MnO_2 + SO_2 = MnSO_4.$$

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We have a direct formation of manganese sulphate. Is that correct?

M. Yes; at least in the main point. Here is some paper which I coloured brown by moistening it with potassium permanganate and then washing it: if I draw on it with a solution of sulphurous acid I at once obtain white lines. In the laboratory this oxidizing effect is employed to estimate iron, i.e., the ferrous ion. The reaction is:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Write the ion equation.

P. I do not quite know how to do it.

M. You have to consider what ions are present, and what valencies are the same on both sides, and so are not altered during the reaction. First of all, break up all the salts and acids into their ions.

P. $10Fe^{\cdot\cdot} + 10SO_4'' + 2K^{\cdot} + 2MnO_4' + 16H^{\cdot} + 8SO_4''$
$= 10Fe^{\cdot\cdot\cdot} + 15SO_4'' + 2K^{\cdot} + SO_4'' + 2Mn^{\cdot\cdot} + 2SO_4'' + 8H_2O.$
Yes; I can cancel some of the factors, and then I obtain:

$$10Fe^{\cdot\cdot} + 2MnO_4' + 16H^{\cdot} = 10Fe^{\cdot\cdot\cdot} + 2Mn^{\cdot\cdot} + 8H_2O.$$

M. You can make it shorter by dividing by two.

P. To be sure; this gives me:

$$5Fe^{\cdot\cdot} + MnO_4' + 8H^{\cdot} = 5Fe^{\cdot\cdot\cdot} + Mn^{\cdot\cdot} + 4H_2O;$$

this, of course, is much simpler.

M. And also more easily understood; for it says: five ferrous ions are oxidized by one permanganate ion with the co-operation of eight hydrogen ions to five ferric ions, and, at the same time, one manganese ion and four water are formed. Now let me show you how we discover when all the iron has been changed from the ferrous to the ferric condition. If I pour a solution of potassium permanganate

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into a ferrous sulphate solution mixed with sulphuric acid, the red colour disappears at once, on shaking, and continues to do so, until, after adding a certain amount, the conversion is completed and the liquid immediately becomes red. Of course, when making an actual estimation we employ known or weighed quantities and let the permanganate solution flow in from a burette. (P. 25.) This must be fitted with a glass stop-cock, as the contents would attack india-rubber. In this way, iron, when present as a ferrous salt, can be quickly and accurately determined.

P. But suppose it is in the ferric state?

M. Then we act on the ion by means of some reducing agent (p. 276) which can be easily eliminated when in excess. Metallic zinc is generally employed for this purpose.

35. CHROMIUM.

M. This element is quite new to you. It ought to be studied after iron and manganese for the character of its compounds fits it for this position. As you see, it is a shining metal, fairly white, and of extraordinary hardness. It is fusible only at a great heat, and remains unaffected by the air. It takes the form of large crystals, which can be pretty easily split along their facets. This metal has not been long known, for it could not be obtained in a pure state until lately, owing to its extremely high melting-point. It used to be prepared on the large scale some years ago by the action of aluminium.

P. How did they manage that?

M. They mixed chromic oxide, which has the formula Cr_2O_3, with finely powdered aluminium in the proportion of their combining weights, and set a light to the mixture at one place. Then the following reaction ensued:

$$Cr_2O_3 + 2Al = Al_2O_3 + 2Cr.$$

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If we have a sufficiently large quantity the temperature rises so high that both the chromium and the aluminium oxide melt. The metal solidifies in blocks containing large crystals. It is used to form an alloy with steel, to which it imparts certain advantageous properties,—especially great hardness. Chromium is of no use by itself, as it is too brittle. It remains bright when exposed to air and moisture. As you see, it dissolves in acids, more readily in hydrochloric and sulphuric acid, with an evolution of hydrogen.

P. The solution is blue.

M. That is the colour of the divalent chromium ion, $Cr^{\cdot\cdot}$. It corresponds to the ferrous and the manganese ion. Its salts, however, are much less stable than the ferrous compounds, for they oxidize with extreme rapidity in the air, and act as strong reducing agents. You see, our solution has already turned green, because the divalent chromous ion has changed into the trivalent chromic ion, $Cr^{\cdot\cdot\cdot}$.

P. Do the suffixes -ous and -ic always denote di- and trivalent ions?

M. They do not severally apply especially to these two factors, but to any implying a less and greater degree of valency. Of course, generally, there are only two degrees, and then the -ous refers to the less, the -ic to the greater.—The trivalent chromium salts resemble those of aluminium and ferric iron; in particular, we have a *chrome alum*, just as we have a potash and an iron alum. (P. 275.) Here are some crystals of the chromium compound.

P. Are these really natural? They are so regular that they look as if they had been artificially prepared.

M. Chrome alum, $KCr(SO_4)_2 \cdot 12H_2O$, crystallizes with peculiar readiness in large, regular crystals, which have the same shape as those of the other alums. If we leave them to form by themselves they are not quite regular, because one surface lies along the bottom of the dish, and so that side cannot develop, but remains flat. In order to give

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every surface an opportunity to expand, we must either hang a small crystal on as fine a thread as possible in the middle of the solution, in order that all sides may have the same chance; or we have, from time to time, to turn over the crystal as it lies on the bottom.

P. I would like very much to make one. May I?

M. Yes. Chrome alum is not expensive, but ordinary potash alum will do just as well. First of all, dissolve not too small a quantity in five times its weight of water; a little heat is necessary to effect this. Next morning some moderately sized, but regular crystals will probably have separated out. Filter the solution into a clean glass, place in it the largest and most regular crystal you have, and leave it to stand, covered over with a sheet of paper, where it will not be disturbed and where the temperature keeps as constant as may be. The crystal will develop in proportion as the water slowly evaporates away from the solution. If other crystals form remove your first one into another clean glass, into which you must again filter the solution. You will have to turn the crystal from time to time, so that it may develop uniformly.

P. Yes; I must certainly try my hand at this.

M. It will require some patience. Chrome alum is the best known of the chromium salts. It is largely used as a means of making glue and gelatine insoluble. I cannot explain the details of the effect, since that is a subject which belongs to organic chemistry. It is brought about by a combination taking place between the gelatine and chromium hydrate.

P. I have not yet seen this hydrate.

M. I shall show it to you now. I cautiously add a little caustic soda to a solution of chrome alum; a greyish-green precipitate of chromic hydroxide, $Cr(OH)_3$, is formed. It dissolves in an excess of the alkali hydrate, and the liquid becomes an emerald green.

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P. What has happened?

M. The same as occurred under similar conditions with aluminium hydroxide. (P. 254.) Chromic hydrate can act as a feeble acid, and allows the hydrogen of its hydroxyl to be replaced by metals. This solution is, however, very unstable. If I heat it the chromic hydrate is thrown down as a precipitate.

P. Why do you keep moving the test-tube to and fro above the flame?

M. Because, if I did not the contents would spurt out. When we warm basic solutions in glass they cling to it so closely that the liquor becomes superheated before beginning to boil. Then, when the first bubbles of steam do form they produce so much vapour on account of the excessive heat that the liquid is hurled out. There! I did not pay attention to what I was doing, when speaking to you, and you see what has happened. Some of the solution has been thrown out onto your book. You must neutralize the stain with dilute acetic acid; by this means you change the free caustic soda into the acetate, which has no corrosive action.

P. What a pretty green colour the precipitate has!

M. Chromic hydrate, as well as its anhydride, chromic oxide, Cr_2O_3, which is obtained from it by heating, is used as a paint. The shade of green depends on the method of preparation; and these varieties are of great value to artists, since they are of extraordinary stability, and are affected neither by the atmosphere nor by light. Chromic oxide is found in nature combined with ferrous oxide as *chrome iron ore*, $FeOCr_2O_3$, which serves as a source of other chromium compounds. It resembles magnetic oxide of iron in composition, only we have the trivalent chromium in the place of the trivalent iron. These two compounds also have the same crystalline form, and are thus isomorphous. (P. 290.)

P. Just as chrome alum and iron alum are. Does this

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similarity hold good for all the corresponding compounds of chromium and iron?

M. By no means for all, but for very many. We, therefore, call chromium and iron themselves isomorphous, using the adjective in a wider sense in order to express that their compounds with the same elements have generally the same crystalline form. However, the most important of the chromium compounds are not those of the chromic, but of the chromate ion. I shall follow the process I adopted with manganese, and melt a little of some chromium compound with the alkali carbonates.

P. I see, you here obtain a yellow, not a green.

M. The chromates are yellow, and so are their solutions in water. But when I add an acid the colour changes to a yellowish-red.

P. That reminds me of the mineral chameleon. (P. 290.)

M. In this case, however, the circumstances are quite different. Here is some potassium chromate, it is a yellow salt, with the composition K_2CrO_4, and so is similar to potassium sulphate and potassium manganate. These three substances have, moreover, the same crystalline form. If I heat some of the dry salt in a test-tube it turns a vivid red. On cooling it becomes yellow again.

P. What causes this?

M. Nothing particularly out of the common. You know that a body has a yellow appearance if it absorbs the violet light-rays. When we heat this substance we cause it to take up more and more of the blue and green rays, and that accounts for the change of colour. Just as the temperature affects certain properties, such as the volume, so, in this case, it alters the capacity to absorb light.—Potassium chromate dissolves easily in water, forming a bright yellow solution, which owes its colour to the chromate ion, CrO_4''. This is similar, in many respects, to the sulphate ion. What is the test for the latter?

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P. The barium ion. A white precipitate is formed.

M. If I bring a barium ion into my yellow solution, say by adding barium chloride, I obtain a precipitate. It is, however, not white, but bright yellow. Barium chromate, $BaCrO_4$, is just as difficultly soluble as barium sulphate, only it differs from the latter by dissolving in hydrochloric acid, as you see.

P. And we get a yellowish-red solution, like what you obtained before.

M. A new ion has been formed; I shall explain what it is directly. If we treat potassium chromate with an acid, and allow the product to crystallize out, we obtain this red salt which I have here and which has just been produced in our solution. When powdered it is yellow, not like sulphur, but orange-yellow, like its solution. Analysis shows that it has the composition $K_2Cr_2O_7$. It is, therefore, the potassium compound of a new anion, Cr_2O_7, which is called the dichromate ion; and, consequently, the salt itself is known as potassium dichromate.

P. How has this been produced from the chromate?

M. You should answer that question yourself. Write the equation showing the action of sulphuric acid on potassium chromate.

P. $2K_2CrO_4 + H_2SO_4 = K_2SO_4 + K_2Cr_2O_7 + H_2O$. Yes; that seems all right. I see, water is also formed.

M. I must show you one other experiment before explaining the action of an acid on the chromate solution. When I add strong sulphuric acid to a concentrated potassium dichromate solution I obtain a glittering precipitate, red like cinnabar. This, in the pure state, has the composition CrO_3. It is the anhydride of chromic acid.

P. Can we not here trace a similarity to sulphuric acid? SO_3 is its anhydride; H_2SO_4 is the acid; therefore, chromic acid must be H_2CrO_4.

M. Quite so. Only this acid cannot exist. It is quite

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certain, from the composition of the yellow salt, that there is a chromate ion, CrO_4'', corresponding to the sulphate ion, SO_4''; but if we try to prepare the acid we only obtain the anhydride, just as happened in the case of the carbonic and sulphurous acids. Here is a larger quantity of this chromium trioxide or chromic acid anhydride. It is now manufactured and sold on the market for industrial purposes. It is in the form of dark red, shining, crystalline needles.

P. But what has this to do with the red potassium dichromate?

M. We can consider the dichromate ion, Cr_2O_7, as a compound of the chromate ion and chromium trioxide: $CrO_4'' + CrO_3 = Cr_2O_7''$; and now you see why it is produced whenever the chromate ion is brought in contact with chromic acid, i.e., whenever we make a chromate solution acid. We can, therefore, simply write the equation with the hydrogen ion:

$$2CrO_4'' + 2H^{\cdot} = Cr_2O_7'' + H_2O.$$

P. And if we make the liquid basic?

M. Then the chromate ion is reformed. For the hydroxyl converts the dichromate ion into the chromate ion and water. Write the equation.

P. $Cr_2O_7'' + 2OH' = 2CrO_4'' + H_2O$. Yes; that's it. These equations are really wonderful!

M. Let us make the experiment. I have here the yellowish-red solution of the dichromate; I add a little sodium hydrate or ammonia—

P. And the liquid turns bright yellow.

M. We shall now leave chromium. I will just show you one other reaction to illustrate its technical importance. I have here a sheet of paper coated with a mixture of coloured glue and potassium chromate, and dried in the dark. I place one half in a book and allow the sun to shine on the

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portion which juts out. After some minutes I remove the paper and wash it in warm water. The glue dissolves only where it had been protected by the book, and not at those places which had been exposed to the sun. This provides us with the means of copying many varieties of pictures. We lay them on paper prepared in this way and let the light penetrate through them.

P. What a wonderful effect! Please explain it.

M. I have already told you that a chromic salt has the property of making glue insoluble. (P. 296.) Well, on exposure to light, glue and many other organic substances act on the chromate in such a way as to deprive it of some of its oxygen and convert it into chromic oxide. This unites with the glue and renders it insoluble. Rubber behaves in the same way; so paper painted with coloured rubber and potassium chromate also gives a photographic impression. The carbon-printing process depends on this effect.

P. I should like to make some experiments with these mixtures.

M. That will not be difficult. In order to prepare the paper you can take any proportions you please. A suitable subject to copy is a pressed leaf, showing the veins prettily marked, or some other object of the same nature. It is laid on the paper, and both are held firmly together by some convenient method between two sheets of glass. In sunlight a few minutes exposure is necessary; and in the shade, from one quarter to half an hour. Of course, in winter several hours exposure might be required; because the weaker the light the longer does the process take.

P. Must I prepare the paper in absolute darkness?

M. By no means. You can work in the evening by lamp-light. Only the drying must be done in some dark place, such as a large, empty box; but be sure that no light can find its way in. Exposure to daylight for a few seconds

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would do no harm; but any longer interval might render a photographic effect impossible by making the whole coating insoluble.

36. COBALT AND NICKEL.

M. The metals which we are about to study to-day show chemical properties which place them on the opposite side of iron and manganese from chromium. In the case of the latter, the highest oxidation products, the chromates, are its most important and most stable compounds; while those of cobalt and nickel which show the lowest proportion, namely, those corresponding to the ferrous and chromous compounds, are the most characteristic. To begin with, here is a piece of metallic cobalt. What does it look like?

P. It is rather grey, perhaps slightly brighter than iron. It appears very firm and tough. I can see no signs of rust or any other action.

M. Good. Cobalt is almost unaffected by the atmosphere. It melts with difficulty, but at a lower temperature than chromium, iron, and manganese. It is of no special use in the metallic condition. It dissolves in acids, with evolution of hydrogen, though only very slowly. Nitric acid, however, dissolves it easily. Do you know why?

P. Because the hydrogen is not given off, but forms water with the oxygen of the nitric acid.

M. Right; and, therefore, in this case, lower oxides of nitrogen evolve. Look how easily the metal dissolves in a warm solution of dilute nitric acid. The liquid has a red appearance.

P. Is that the colour of the cobalt ion?

M. Certainly. We have produced a solution of cobalt nitrate, $Co(NO_3)_2$; and this contains the cobalt ion, $Co^{\cdot\cdot}$. All its salts show this same colour in a dilute solution. On the other hand, when more concentrated, in which case the compound is only partially broken up into its ions, we can see all sorts of other colours, more especially blue. These

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tints are those of the undissociated substance. The nitrate is the best known and most used of the salts of cobalt. We also have the chloride, $CoCl_2$, which crystallizes with $6H_2O$, and the sulphate, $CoSO_4$, which contains 7 molecules of water of crystallization. All these compounds are red when in the crystalline state; but several become blue on removing the water.

P. I think I have a blue pigment in my paint-box, called cobalt.

M. Yes; this is generally a cobalt glass, i.e., a silicate of cobalt and sodium. That dark blue glass, of which they make vases and stained window-panes, is coloured with cobalt. If we use just enough of this metal as will make the silicate powder blue we obtain a pigment unaffected by the light and atmosphere. The finer varieties are used in painting.

P. I saw something one evening, a short time ago, which surprised me. A carriage-light looked red from a distance; but as I came nearer I found that both it and the glass in the lamp were blue.

M. Then it was a cobalt glass; and on examination you would find that not only blue, but red rays also, pass through it without being absorbed. Therefore, the light is rather more violet than blue. When there is a slight haze in the evening, the red beams can penetrate much further than the blue; and this was why the light you saw shining in the distance through the mist had a reddish appearance. Besides, the carriage lamp was probably burning somewhat smokily; that would cause a show of red light to preponderate, and this effect would be all that would reach you when you were far away. But, on coming close up, the blue rays would be so strong as to make the red imperceptible.

P. Yes; it might very well have been as you say; for I have only observed this peculiarity occasionally but not always; that may have been because it was not always misty.

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M. When you next have an opportunity note if your surmise is correct. And now let me show you how the red can change into the blue salt in a manner which used to cause much surprise to the early chemists. I draw some strokes on a sheet of paper with cobalt chloride solution. I must not use a steel nib for this purpose, because the iron would decompose the liquid. When the lines are dry they are scarcely visible, for the red is so pale; but on warming the paper cautiously—

P. They have turned a beautiful blue colour! What a pretty experiment! I say, have those artificial flower barometers by which we foretell the weather, anything to do with cobalt? When they are red, it is going to rain; when they are blue, it will be fine.

M. Yes. They consist of some white fabric which has been saturated with a concentrated solution of cobalt nitrate. If the air is dry, the salt loses water and changes into the blue compound, and this, in a damp atmosphere, absorbs moisture again and turns into the red crystals.

P. Then are they correct weather prophets?

M. They cannot predict atmospheric conditions; all they do is to give some indication of the amount of moisture actually present in the air. However, if the air is damp, and there is no rain, the probability is that we shall have wet weather before long, at least sooner than if the atmosphere is quite dry. And so, after all, they thus enable us to make a better guess as to how the day will turn out.—I shall now show you cobalt hydroxide. How is it prepared?

P. Oh! I ought to know that by this time. By adding the hydrate of potassium or of sodium to a solution of a cobalt salt. The product is thrown down if it is insoluble. May I make the experiment? Yes; there is the precipitate; it is bluish green.

M. Good. That is practically all I have to tell and show you about cobalt. It has a large number of compounds,

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but they are of such complicated natures that it would take up too much time were I to explain them to you.

P. Are there no higher oxides of cobalt?

M. Yes; there is a very unstable one, Co_2O_3, which corresponds to ferric oxide; and another, Co_3O_4, which is even more unstable and may be compared to magnetic oxide of iron. This latter compound of cobalt is used, in the form of a black powder, as a pigment for porcelain.

P. Does it make the porcelain black?

M. No; blue. It melts with the silicates in the glaze and forms a blue glass (p. 303). As it dissolves in the heat the colouring-matter generally penetrates down from the place where it has been applied, and gives the near vicinity the same appearance as when dried ink has become wet and has run. This blue lustre is often seen on porcelain ware.—We now come to nickel. The small coinage of Belgium, Germany, and the United States contains this metal. It is of much more use than cobalt since it is harder, is more capable of resisting air and moisture, has a beautiful yellowish-white colour, and takes a good polish. It is employed sometimes in the pure condition as a coating on other metals.

P. Ah! You refer to nickel-plated objects, the handle-bars of bicycles and such like. You often hear of galvanized nickel-plating; what does that mean?

M. It means that the nickel is precipitated onto the metallic foundation by an electrical process.

P. Then it is the same as nickel electroplating?

M. Yes. Galvani was the man to whom we owed the first observations regarding the electric phenomena resulting from the contact of metals with liquids. Before his time we knew only of the electricity produced by friction and by lightning. Therefore they distinguished this latter form of electrical decomposition as galvanic, and its study as galvanism. However, Galvani's theories on the subject were somewhat erroneous; they were improved upon by Volta;

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and, eventually, Ritter and Faraday showed them in their true relationship to chemical phenomena.

P. I would like to have more information about these matters.

M. Many accounts of these discoveries have been written; you can study them later on. To-day we shall confine ourselves to the essential points in connection with galvanizing. You know how an electric current passes through an electrolyte?

P. The positive electricity travels with the cathions, and the negative with the anions.

M. Right; and what happens where the current leaves the electrolyte and enters the electrode?

P. The ions remain behind, while the electricity passes on by itself.

M. Quite correct. But a metallic ion, deprived of its electricity, is just the metal in its ordinary condition. So if we take a conducting material as a cathode all the metallic ions travel to it, and the metal separates out and forms over it a coating, which becomes thicker the longer we allow the current to pass. If the material is clean and well polished this coating will stick very firmly to it. That is the method we adopt in plating with gold, silver, copper, and nickel, also.

P. I would like to see this process.

M. I will show it to you later on, when we come to copper, which was the first metal to be employed for this purpose on a practical scale. However, electroplating is not the only method of obtaining a coating of nickel. We can lay nickel-foil on a sheet of some other metal, especially steel, and make them unite by using pressure; very durable material is produced by this means. In addition, nickel can be alloyed with many other metals; with iron we obtain *nickel-steel*, a mixture yielding valuable properties. Nickel hardly dissolves at all in dilute acids; but quickly in nitric acid, just as cobalt does.

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P. May I try? Yes; it dissolves right away. The solution looks as if it were turning green.

M. Yes; nickel nitrate, containing the green nickel ion, $Ni^{\cdot\cdot}$, has been formed. The solid salts, which all separate out from their solutions with water of crystallization are also coloured green, not pale, like the ferrous compounds, but a beautiful pure green. In the water-free condition, most of them are yellow. Here is the sulphate. It is the salt usually employed in the nickel-electroplating process.

P. Let me make the hydroxide. It is bright green.

M. Now try with ammonia, instead of caustic soda.

P. I ought to obtain the same precipitate. Yes; there it is.

M. Add some more ammonia.

P. What difference will that make? Hm! The solution has become dark blue and everything has dissolved. What has happened?

M. Since the green colour has disappeared we must conclude that the nickel ion is no longer present. It has combined with an excess of ammonia and formed a blue ion of the composition $Ni(NH_3)_4^{\cdot\cdot}$.

P. How do you know that?

M. Because from the solution we can obtain a solid salt which, supposing we started, as in this case, with the sulphate, has the formula $Ni(NH_3)_4SO_4$. However, this compound is of no special importance. I only brought the point to your notice because such combinations of ammonia with the ions of the heavy metals occur very frequently.—In conclusion, I shall just mention that a compound of nickel containing more oxygen than corresponds to a divalent condition can be prepared, but it is even more unstable than the analogous cobalt oxide. Nickel therefore behaves, on the whole, as a divalent element, like magnesium and calcium, and differs, in this respect, from most of the heavy metals; for, as you have seen, they, as a rule, form many groups of compounds,

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each different in valency. On the other hand, zinc, which we shall study to-morrow, is more simple in its combinations.

37. ZINC.

M. You are already acquainted with this metal in daily life. What can you tell me about it?

P. It is white and not very hard. It remains bright in a damp atmosphere, and dissolves easily in acids with evolution of hydrogen.

M. Yes. Its melting-point, 420°, is much lower than those of the metals which we have just been considering. if we heat it strongly in the air it burns with a bright flame to its oxide. On being warmed apart rom oxygen it boils at 950°.

P. Can zinc really boil?

M. Certainly; just as mercury can. Indeed, we have been able to measure the vapour density of zinc, and have thus found that its molecular weight is 65. Its molecular and combining weights are, therefore, the same, and the formula for zinc vapour is Zn.

P. That is by no means the case with the elements which we have come across so far. They always had two or more combining weights in one molecule.

M. Zinc does not stand alone in this respect; for every other metal, whose vapour density we have been able to examine, has shown this same peculiarity. We knew long ago that the molecular weight of mercury was expressed by the formula Hg, not Hg_2 or Hg_4. We are not yet aware of the reason of this characteristic.—You know that zinc is used for all sorts of purposes.

P. Yes; pails, roofing, etc., are made of it.

M. That is because this metal resists oxidation fairly well in damp air. To be sure, it is more easily attacked than iron; but the coating of oxide formed over it sits firm, as it does in

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the case of aluminium, and provides a good shield to the metal lying beneath it. Indeed, we cover iron with zinc in order to protect it. Such "galvanized" iron is of special use for agricultural implements, wire fencing, and the like.

P. Does "galvanized," as used here, have anything to do with electricity?

M. Yes; in a certain sense. I have already told you that if two different metals are simultaneously in contact with a conducting liquid, an electric excitement (in most cases a current) is produced. This causes electrolysis to ensue, by which means one of the metals is oxidized; in the case of zinc-iron, it is the zinc. The iron, owing to its zinc coating, is better able to withstand the electrical attack of water and oxygen, because the latter metal can resist these better. I shall soon refer to this matter again, so leave any question till then.—In addition to its use as a protective jacket, zinc is also employed as an alloy with other metals. Thus with copper it forms *brass;* while *nickel-silver* or *German silver* contains nothing but copper, nickel, and zinc.—Here is some zinc dust, a peculiar form of the metal.

P. Is this really a metal? It is quite grey in appearance, and has no metallic sheen.

M. You will at once notice a glitter if you grind the powder in a mortar.

P. How is it obtained in this condition?

M. This variety is produced spontaneously during the preparation of the metal, which has to be distilled, since, as it is volatile, it cannot be melted like iron or copper. The fractions which come over first condense as a powder so long as the receiver keeps cool. However, when the temperature has risen above 420° the distillate collects in drops and we obtain a coherent mass. We make use of this dust when we require a reducing agent capable of providing a large surface area. For example, it provides a rapid means of reducing the ferric ion to the ferrous state for purposes of

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analysis. (P. 294.) Thus, ferric chloride solution, if shaken up for a short time with this finely divided zinc, becomes colourless. You can make the experiment afterwards for yourself.

P. Yes; and I shall use red prussiate of potash (p. 287) to test if all the ferric ions have really been reduced.

M. Good. You must have already noticed that solutions obtained by the action of acids on zinc have no colour. They contain the colourless divalent zinc ion, $Zn^{\cdot\cdot}$, which resembles those of ferrous iron manganese, and magnesium. Of its salts we have the sulphate, $ZnSO_4 + 7H_2O$. This is a white substance, very soluble in water. It is of varied use, both in medicine and the manufactures. Here is the chloride, $ZnCl_2$, which is extremely easily soluble in large quantities in water. It is employed for many purposes. Railway sleepers are sometimes impregnated with it, as it serves to protect the wood against fungus and other destructive living organisms.

P. How does it do that?

M. Because the zinc ion acts as a poison; and though not a particularly strong one, its effect is quite sufficient to kill such growths as these. A solution of the salt is also serviceable in soldering, just in the same way and for the same reasons as sal ammoniac is. (P. 225.)

P. Let me make this metal's hydroxide, also. There it is! It is white, as are all the other zinc compounds. Ah! I have made a discovery! It dissolves in excess of caustic soda.

M. Now try and explain why.

P. Is it because zinc hydroxide, like the hydrates of aluminium and chromium, can act as an acid?

M. Certainly. Zinc salts, moreover, on treatment with ammonia, first give a precipitate of the hydroxide, which then dissolves in excess of the base, as you see. However, this is due to another cause. What is it? Nickel behaved in the same way.

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P. The nickel ion unites with the ammonia, and forms a new cathion. But if a similar reaction occurs in the case of zinc we ought to have a change of colour; now, this liquid is water-clear, as it was before.

M. Your solution has probably undergone a change of colour, only we have not been able to detect it.

P. I do not understand.

M. You know that the colour of a body depends on what rays of light it absorbs; and you are also aware that, in addition to light rays which we can see, there are other, invisible ones, which differ from the former in having a greater or less number of vibrations. They can be detected by their chemical or heat effects, but not by the eye. Well, if a body absorbs these invisible rays we perceive no alteration; because all the light rays, which alone make vision possible, pass through. And, therefore, we can see no difference, if the rays remain in the invisible form, even though they are altered by the chemical change.

P. Yes; I understand that this might be so; but can you prove it?

M. To be sure we can. Namely, by examining the nature of the invisible light with suitable apparatus. It has not been done in this particular case, but in many other instances our investigations have been brought to a satisfactory conclusion. What made us consider that the zinc formed a complex zinc ammonia ion was the fact that compounds of this nature are known in the solid condition.—When zinc hydroxide loses water it changes into the oxide, ZnO, a snow-white powder, which can be prepared directly from the metal, by heating zinc in the air. It is used as a pigment, under the name of *zinc white.* Let us now give some attention to zinc sulphide. Do you remember it?

P. Oh! Yes! It was the white precipitate which we obtained on adding hydrogen sulphide to a zinc solution. Of

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the other metallic sulphur compounds then prepared it was, I recollect, the only one of that colour.

M. Yes. Zinc is the only one of the heavy metals (at least of those known to us) whose sulphide is white. This enables it to be easily detected in analysis. However, the salt is also of interest as being the most prevalent ore of zinc. It is called by mineralogists *zinc-blende*. Here are some pieces.

P. But they are a yellowish brown, not white.

M. That is caused by impurities, especially iron, very small quantities of which are sufficient to mask the whiteness of the zinc sulphide. In order to obtain the metal we have to roast the ore. Do you know what that means?

P. You once told me. I think it means that it is heated.

M. Not only that, but heated in such a way that the air has free access; in fact, it denotes an oxidation at a high temperature. What is the result of such a process?

P. Ah! Now I see. The sulphur burns away as the dioxide, and the metal is at the same time converted into its oxide.

M. Yes. Write the equation.

P. ZnS+—let me think; zinc requires one oxygen, and sulphur takes two; that makes three; so,

$$ZnS+3O=ZnO+SO_2.$$

I remember now that you told me that this sulphur dioxide was made into sulphuric acid.

M. Yes; partly for economy, and partly because they are not allowed to let the sulphur gases escape into the air, since they—

P. —injure plants.

M. Right. In order to convert the zinc oxide into the metal charcoal is added, and the mixture is heated in retorts. But these are not like ordinary retorts; they are made of burnt clay, either in the form of cylinders, closed at one end, or large boxes. Several of them are built into one oven, and all are heated at the same time.

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P. The vapour given off from them condenses first as dust, and then as a liquid?

M. Quite right. In addition to zinc-blende carbonate of zinc is also found in nature. It is called *calamine* or *zinc-spar*, and is another crude source from which the metal is obtained. How could we make zinc carbonate itself?

P. By treating zinc hydrate with carbonic acid.

M. That would not be a good method, because the hydrate is such a feeble base that it would only unite with the carbonic acid (or rather the carbon dioxide) with difficulty. How do we tell if a base is of this nature?

P. If its salts give an acid reaction; that shows they have been partially split up by water, and therefore the hydrate must be a weak base.

M. Good. You can afterwards test a solution of zinc sulphate with litmus, and convince yourself that it has acidic properties. We prepare the carbonate by bringing together the dissolved zinc and carbonate ions. It is then obtained as a precipitate, since all the carbonates of the heavy metals are insoluble in water.

P. Then does the insoluble salt always separate out in such cases?

M. I think I once told you that, if neutral, they invariably did so. The salt which is least soluble is always the one that precipitates from a solution containing ions of different kinds; provided, of course, that the ions thus separating out, are in excess of the quantity necessary to form a saturated solution. You remember how I mentioned that 1 litre of water can dissolve 0.0015 g. of silver chloride; it depends on whether we have a greater or less percentage of chlorine and silver ions present whether we obtain a precipitate of silver chloride or not. Well, then, we take some zinc ions, say a solution of zinc sulphate, and some carbonate ions, say a sodium carbonate solution, and mix both together.

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P. You have obtained a white precipitate.

M. Yes; that is the zinc carbonate. It behaves in the same way as magnesium carbonate (p. 250), since both the base and the acid are weak the water effects a partial decomposition of the salt. Therefore, this product does not consist of the pure carbonate alone, but has some of the hydrate mixed with it. How can we prepare the oxide from the carbonate? Think of calcium carbonate.

P. By simply applying heat. The equation is:

$$ZnCO_3 = ZnO + CO_2.$$

M. Yes; that's the way. It is an easy process. Here is a little white carbonate of zinc. I heat it in my porcelain crucible. Look inside!

P. The contents have turned yellow. There can be no zinc oxide there.

M. Examine the powder again now that I have removed the flame.

P. I do not see anything very special. Ah! It appears to be getting paler. It is now white.

M. Here you have an example of what I spoke of before. (P. 311.) Zinc oxide, when cold, absorbs certain invisible rays which lie beyond the violet vibrations; but when heated the character of the absorbed light changes more and more into the visible, violet form, and when this is removed from white light we obtain—

P. —a yellow colour. I understand that all right, it is the invisible rays that confuse me.

M. You now know how we prepare the oxide from the carbonate of zinc ore, and you have also been told how the metal itself is extracted from its oxide. I shall just add that zinc is much used for the production of electricity from chemical energy. I must postpone entering into details on this subject till our next lesson.

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38. COPPER I.

M. To-day we have to do with copper. It is a metal which was familiar to man probably before any of the others; for, in the first place, its natural compounds are numerous and easily reduced to the metallic condition, and, secondly, free copper is occasionally found in large quantities. It may be looked upon as representing the transition stage between the base and noble metals.

P. You said just now that it was fairly abundant, therefore we cannot call it a noble metal.

M. This designation does not imply that a metal is rare, but that it resists the action of air and water. Of course, silver and gold, which remain unaffected whether the temperature is high or low, possess this power of resistance and, at the same time, happen to be scarce; but, in a chemical sense, a noble metal is one which is disinclined to enter into combinations.

P. That is to say, it is too proud?

M. Not so; it is not a matter of will, but of necessity; the metal is incapable of behaving otherwise than it does. Owing to the prevailing conditions, due to a definite proportion of oxygen in the atmosphere and a slightly variable temperature on the surface of the earth, different metals act in different ways. On the sun, where the heat probably reaches 6000°, we would perhaps have to apply the adjective "noble" to quite other metals.

P. Which would they be?

M. We cannot tell, for 3000° is the highest temperature at which our experiments can be carried on, and it would serve no purpose to advance conjectures which we cannot prove.—Well, copper is not a noble metal, since it oxidizes both in the heat and in damp air. However, under ordinary conditions, this reaction goes very slowly and almost ceases as soon as a layer of oxide has been formed. So, after all,

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copper may be said to behave well in this particular respect. That is why it is used to cover the roof of any valuable building, such as a church; it may then be easily recognized by its bright green colour.

P. Why is it green?

M. Generally, owing to the formation of a basic carbonate. We shall refer to this substance later on. Again, copper is employed to sheath ships, because it makes a good resistance to sea-water which is much more destructive than fresh water to metals. And, of course, you know copper as coin of the realm, for which it is suitable both for its permanent qualities and its intrinsic value. Its actual colour is seldom apparent, because of a thin and rapidly formed coating of oxide; but if this is removed, say by hydrochloric acid, the true nature of the metal is seen. Look here!

P. It is by no means copper-red, but has rather a rose tint.

M. Yes. What we call copper-red is the colour of the rusty, not of the pure, metal. Copper melts at 1050°, and is fairly ductile, although not very hard. It has a special electrical property in being one of the best conductors of electricity, and is used in large quantities on this account.

P. I do not exactly understand what that means.

M. You know that electric energy can be conducted anywhere through metals, but it has, as it were, to pay a toll on the way. In other words, all the energy is never given up at the end of the journey; a portion always remains behind in the conductor and is changed into heat. This remnant is less the thicker the conductor is, and also varies with the nature of the conducting material. For example, an iron wire must be seven times as thick as a copper one in order that a current of definite strength may pass through either with the same loss of energy. We therefore say that copper conducts seven times as well as iron.

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P. Then is there no perfect conductor which does not possess this disadvantage?

M. Well, the colder a metal is the better does it conduct. We could work with much thinner wires if we could immerse them in liquid air; but that is impossible in practice.—Let us now refer to some of the other properties of copper. It does not dissolve in dilute acids, i.e., it is incapable of displacing the hydrogen from them.

P. Then can hydrogen displace copper?

M. Certainly; but only under special conditions. If a copper solution is enclosed with hydrogen, in the presence of platinum, the metal soon separates out and the corresponding acid is produced.

P. What part does the platinum play?

M. It hastens the reaction, just as it does in a mixture of oxygen and hydrogen; in other words, it acts as a catalytic agent. If we take copper sulphate, the equation is:

$$CuSO_4 + H_2 = H_2SO_4 + Cu.$$

Should you wish to see the experiment, stick a small piece of platinum foil firmly into a test-tube, fill it with a solution of sulphate of copper, and then pass in hydrogen until the foil dips into the liquid, as in Fig. 31. After a day or so, you will find that the hydrogen has become less, while red copper has separated out onto the platinum. This must be cleaned, by igniting it, immediately before the process; otherwise the reaction goes too slowly.

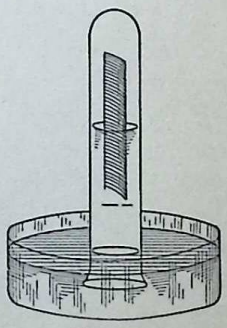

FIG. 31.

P. Would the salts of zinc and the other metals which make hydrogen evolve not give the same result?

M. No. In this connection we can arrange the metals in a definite series, in which hydrogen may also be included, because it, like them,

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can form a simple cathion. I have here a silver solution; I throw in a piece of copper. What do you see?

P. A grey growth forms over the copper, and the liquid turns greenish.

M. Yes; the silver salt has changed into the corresponding copper compound. The grey precipitate is metallic silver. I pour off some of the solution, and throw some zinc into it.

P. A black substance separates out, and the liquid becomes colourless.

M. The copper has now been displaced by the zinc. The equations are:

$$2AgNO_3 + Cu = Cu(NO_3)_2 + 2Ag,$$

and

$$Cu(NO_3)_2 + Zn = Zn(NO_3)_2 + Cu.$$

You see that the nitrate ion remains unchanged; it has to be there only in order that the metallic cathions may be present, but any other anion could be used in its place. Practically, as far as we are concerned, the reactions might be represented thus:

$$2Ag^{\cdot} + Cu = Cu^{\cdot\cdot} + 2Ag,$$

and

$$Cu^{\cdot\cdot} + Zn = Zn^{\cdot\cdot} + Cu.$$

P. Then it just depends on the relative strength of a metal whether it retains its dots or not. A strong metal will always remove them from a weak one.

M. Quite right. Ion equations, such as these, may be considered as representing a complete change, because the special effect in one particular direction is so powerful. These dots correspond, as you know, to charges of positive electricity (pp. 96 and 285); thus you can say that metals possess this form of energy in different degrees. In fact, we are able to tabulate all the metals in such an order that each one is stronger than those which follow, and so can expel them from their salts. For if a metal, A, drives out another, B,

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which, in its turn, can displace C, then A can also drive out C. Experiments have showed that this deduction always holds good. Such a grouping is known as a table of electric potentials, because it is drawn up according to the electric pressure observed between the various metals when they dip simultaneously into a watery solution. This is the essential principle underlying all forms of galvanic, or rather voltaic, cells.

P. Will you explain them to me in detail?

M. With pleasure; for you have now got the length of being able to understand them. I shall set up a Daniell's battery, so called after an Englishman who discovered this method in the middle of the nineteenth century. I pour some zinc sulphate solution into a glass vessel, and place in it a solution of copper sulphate contained in a jar of unglazed clay through which liquids can indeed penetrate, but only very slowly. A sheet of zinc, attached to a wire, dips into the zinc sulphate, and a piece of copper, similarly attached, is immersed in the copper sulphate. If I now fasten the two wires to the binding-screws of an electrometer or galvanometer the needle begins to move, showing that an electric current is passing.

P. This seems just like the battery which I have at home. (P. 100.)

M. Yes; the principle is the same, but not so easily understood. If we connect the two conducting wires and thus make a current pass through our battery, we find, after some time, that the zinc has partially dissolved, while the copper is covered with a coating of fresh rose-red copper. In fact, the same chemical action has ensued as when we threw the zinc into the sulphate of copper solution; the zinc has dissolved, and an equivalent quantity of copper has separated out.

P. Yes; so I see. But why is it that, in the battery, we obtain an electric current and not an ordinary precipitate?

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M. Because we have so arranged that the zinc does not come in contact with the copper solution.

P. Yes; I had thought of that; but then, how is it possible to have any precipitate at all?

M. Just because it is produced by the electric current. I see you do not understand, so I will show you what happens. Metallic zinc has, as you know, a strong tendency to change into its ions; for, in order to do so, it will decompose not only copper salts, but hydrogen salts or acids. In this process it has to absorb positive electricity; and does so by withdrawing some from the conductor to which it is attached. The conductor tries and manages to repair this loss by removing, with the aid of the piece of copper, the positive charge from an amount of copper ion equivalent to the zinc dissolved. Owing to this change the cathions in the zinc division of the battery increase in quantity, and those in the copper division becomes less. In order to balance this inequality a corresponding amount of sulphate anion travels through the clay cell from the copper to the zinc side. This regulates the electric and chemical conditions sufficiently to enable a repetition of the process, above described, to take place. As a result, we obtain, on the one hand, a constant electric current which flows through the conductors or wires from the copper to the zinc, and, on the other hand, a dissolving away of the zinc and an equivalent precipitation of the copper. This continues so long as both metals are connected by some conductor of electricity, or until either all the zinc or all the copper ions are used up.

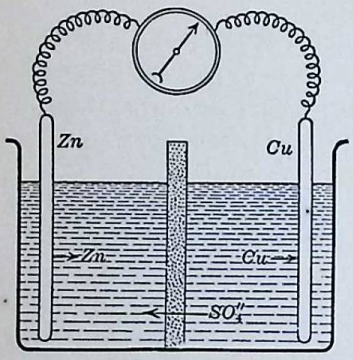

FIG. 32.

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P. Hm! I think I understand. The zinc would like to precipitate the copper, but cannot reach it except by the electric current, and therefore it makes the current.

M. Quite right. When you compress air into a popgun it has a strong tendency to expand, but it cannot do so without driving out the cork. Many another similar instance will occur to you. The voltaic battery is a machine for making electricity out of chemcial energy. Therefore, you must arrange matters so that this chemical force is not expended other than in performing electric work. On that account the zinc has to be separated from the copper sulphate solution, and both must be united by some conductor of electricity.

P. Yes; I understand. But there are a great many things I would like to know. In the first place, could we take other metals instead of zinc and copper?

M. To be sure we could. By immersing each metal in a solution of its salt, we can set up a voltaic cell with any two metals we please. Only the strength of the current would vary with the metals taken, i.e., the amount of work done would be different.

P. Why?

M. Let us refer to our old example. If the metal A can precipitate the metal B from its salts, and if B has this same effect on C, then A has also the power to expel C. Well, supposing we begin by working a battery with A and B, then A dissolves and B is thrown down. Let us now make a cell with B and C; in this case B is dissolved and C precipitates. Both taken together come to the same thing as if C were directly decomposed by A; for B was first dissolved, then precipitated, and lastly was again put into solution, and therefore ends in the same condition as when the operation commenced. Consequently the two cells together afford just as much work as the A and C cell by itself; therefore, the A-C couple is as strong as the A-B plus the B-C couples.

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P. I can quite understand that; but how is the strength of the couple measured?

M. By what is called the pressure or potential. (P. 74.) You now see the origin of the term "table of electric potentials." In order that a battery may do work one of the metals must precipitate the other; if you had the same metal in the same solution in both divisions, there would be no inducement for the production of a current.

P. Yes; I see that. So we can make batteries with metals and their salts. Is there any other method?

M. Yes; the dissolving of the zinc corresponds to an oxidation, the precipitation of the copper to a reducing process. We can produce electricity by connecting any oxidizing agent by means of a porous cell with some reducing agent. But we must introduce a conductor before the current will pass. For this purpose we place in each liquid a piece of platinum foil or a rod of carbon (since neither of these elements is liable to be attacked). For example, I might have a solution of sulphurous acid in the outer division, and one of potassium chlorate with some hydrochloric acid in the inner. If I then dipped a platinum disc into each and bound the wires attached to them to an electrometer, I would obtain a current which would cause the needle to move.

P. I have a sort of general comprehension of the position, but can you not explain more exactly how the electricity is produced in these cases?

M. I could enter into further details, but they would lead us too far. We have, so far, hardly touched on copper itself and its chemical behaviour. We must overtake that subject to-morrow.

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39. COPPER II.

M. Up till now, I have found it simpler to call the greenish-blue, divalent cathion of copper the copper ion; but now I must tell you that there are two varieties. There is a monovalent ion, in addition to the divalent one which you know. In order to distinguish between the two we use the suffixes -ous and -ic; the divalent is known as the cupric, the monovalent as the cuprous ion. However, the latter is of little importance.

P. So, in this copper differs from iron and chromium. Their compounds were divalent and trivalent.

M. Later on you will find that there are also combinations in still other proportions, sometimes as 2:4 and 1:3. Of the cupric salts you are already familiar with the sulphate, $CuSO_4.5H_2O$. It forms large blue crystals and is the best known compound of copper; it is generally called *blue vitriol.* It used to be used in large quantities for voltaic batteries in the way I described to you yesterday. Now it is employed for the precipitation of copper by the galvanic process, not only to coat articles, but also to produce accurate casts from them. You will understand from what I told you in our last lesson how this is effected.

P. I think I do. We allow the copper ions to travel with the electric current to the place where we wish the metal to be deposited, and then leave them there by conducting the current away.

M. Quite right. This shows you that the object on which the copper is to be thrown down must be a conductor of electricity. If it is not one of itself we must cover it with something which is. We generally use graphite.

P. It must be a pretty process to watch.

M. And it is quite an easy one. I shall, first of all, explain the main principles to you by a simple experiment; you can afterwards try your luck in any other direction you fancy.

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I dip pieces of platinum and copper foil (both of which are fitted with wires) into a copper sulphate solution, and fasten the platinum to the zinc pole of your old dry battery—

P. I am afraid it will be able to do no more work, I have used it so much.

M. I think it will give me as much as I require. I connect the copper with the other pole, and dip both metals into the solution, but do not allow them to touch each other. Now the current passes; the copper ions are led to the platinum and are there deposited as copper. The sulphate ions go in the opposite direction. What effect have they on the copper? Remember what happened before. (P. 98.)

P. Oh! I know. The SO_4 unites with the metal and forms copper sulphate.

M. Quite right; copper is precipitated on to the platinum and the same quantity of fresh copper is dissolved at the anode. The solution always contains a constant proportion of sulphate of copper, and the current has no work to perform other than to drive the metal from the anode to the cathode, and this a weak battery can accomplish. I now take out the platinum—

P. Yes; the red copper is quite clearly visible on its polished surface.

M. By this method we can let the copper deposit on any article we wish. Take the gypsum mould of the coin which we made some time ago. (P. 235.) You had better coat it first with varnish so as to prevent the copper solution from penetrating, then rub graphite on it with a soft lead pencil, fasten it to a copper wire in such a way that the conductor is in contact with the graphite, and proceed as I have just done.

P. That I will.

M. You need not use a dry battery. You recollect that in the Daniell's cell (p. 319) copper separates out, and in the other division zinc dissolves. Therefore, if you substitute

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for the copper plate the object which you wish to coat, or of which you require a cast, you obtain the same result as if you had used a special battery. For the copper is precipitated from the copper sulphate solution by the zinc, and is compelled by the electric current to deposit itself on the place you wish.

P. But the process in the Daniell's battery is not quite the same. There I compel the chemical energy to change into electricity. How does that coincide with the other effect?

M. Both are directly bound up with each other. The electric current is not obtained unless the zinc is kept separate from the copper salt; and, for just the same reason, the copper precipitates on the cathode, and not on the zinc, as it does when both are in immediate contact. Moreover, this precipitation is employed not only for electrometallurgical purposes, but also to purify copper. If the metal comes in a contaminated condition from the smelting furnace, they arrange it in plates face to face with thin sheets of pure copper, and let the current pass in such a way that the impure metal dissolves; it then serves as the anode. Then absolutely pure copper separates out on the copper sheets, for the impurities either remain in the undissolved state and fall as a mud to the bottom, or if they dissolve (as, for example, iron would) they do not separate out at the cathode. This purification is of great service, for slight traces of foreign metals lessen the conductivity of copper enormously. (P. 316.) —Here is another of the cupric salts, the chloride. In the water-free condition, it is a yellowish-brown powder, it crystallizes with $2H_2O$ in greenish-blue crystals. They generally have a green appearance, as they are apt to retain some of the mother-liquor, which is green when concentrated, but blue if dilute.

P. Why is that?

M. In a concentrated solution the dissociation of the cupric chloride is not complete, and therefore the greenish-blue

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colours of the copper ion is not so apparent as the yellow tint of the undissociated salt. But on dilution more and more ions are formed and the solution becomes bluer. Moreover, cupric chloride provides us with a "sympathetic colour" (as we call it) similar to that obtained with cobalt salts. On drawing lines on a sheet of paper, after they have dried, we cannot see the bluish-green of the crystalline salt, but, on warming the dark-yellow water-free compound is produced, and this is clearly visible. By the skillful use of both solutions we can paint a landscape in such a way that, when cold, it looks like a winter's scene, and, on warming, the blue sky, green trees, and yellow meadows give it the aspect of summer.

P. Oh! I must try and paint one!

M. You have not yet seen copper hydroxide, or, more accurately, cupric hydroxide, $Cu(OH)_2$. I obtain it in the form of a bright-blue precipitate by adding some caustic soda to my sulphate of copper solution. Now I apply heat—

P. The hydroxide has become quite dark brown. What has happened?

M. It has changed into copper oxide, which is brown.

$$Cu(OH)_2 = CuO + H_2O.$$

P. It is really very remarkable that the hydrate should be able to lose water when completely immersed in water.

M. Others have also been astonished at this. The fact is that the hydroxide contains no water; but water can be produced from it, as it can be obtained by the explosion of hydrogen in oxygen. In the case of most hydroxides, we have to do work in order to obtain water from them; here, on the contrary, water is formed with the production of energy; therefore, the reaction goes of its own accord.

P. Then, according to that, such processes which perform work are the only ones that take place of their own accord.

M. Certainly; otherwise we would have perpetual motion, i.e., a machine which would afford as much energy

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as we wished without any expense. For if a process takes place of its own accord and work could be done by the reverse reaction, then the desired object would be attained.

P. Hm! Yes; I see that what you say must be correct, still I do not yet quite take it in.

M. Think over the matter afterwards to yourself, and you will soon be convinced.—Copper oxide is also formed when we heat the metal in the air. Here is some polished copper foil; I hold it in the flame—

P. Oh! What beautiful colours!

M. They are caused by the thin layers (p. 265) of oxide and are modified by the red tint peculiar to all copper. The hydrate and oxide of copper are insoluble in excess of sodium hydrate. The former has therefore no acidic properties; it, however, dissolves in ammonia. Just try.

P. The solution is very dark, nearly black.

M. If you dilute it somewhat you will see that it is transparent and of a very beautiful cornflower blue. It contains a new ion, which is composed of the cupric ion and ammonia, and has the formula $Cu(NH_3)_4^{\cdot\cdot}$.

P. This is similar to the nickel compound, and also resembles it in colour.

M. This solution is darker. I add sodium carbonate to a copper solution.

P. A greenish precipitate is thrown down.

M. It is carbonate of copper; however, as with some of the previous carbonates, it is not pure, but has the hydroxide mingled with it. (Pp. 250 and 314.) I show it to you because compounds of a similar composition occur in nature. One is bright green, has the formula $Cu_2(CO_3)(OH)_2$, and is called *malachite.* Another is dark blue, has the formula $Cu_3(CO_3)_2(OH)_2$, and goes by the name of *azurite.* They are made into ornaments of various kinds, and are also a ready source of copper. Now for another reaction: I add some tartar to a copper sulphate solution.

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P. What is tartar?

M. The potassium salt of an organic substance, tartaric acid. If I now pour in hydrate of sodium or of potassium no hydroxide is precipitated, but the solution remains clear and assumes a dark-blue colour, such as we obtained with the ammonia solution. This shows that here again a new ion is formed. I shall not tell you exactly what it is for you do not yet understand organic chemistry and could not follow me. I shall, however, make use of the solution to show you something else. When I warm it with some ordinary sugar nothing appears. But if I take honey-sugar instead—

P. The liquid becomes clouded and looks dirty. Now it clears and a brick-red precipitate is thrown down.

M. So you see that different kinds of sugar can be distinguished from one another by means of the blue solution. The red precipitate is cuprous hydroxide, Cu(OH), the hydrate of the monovalent copper.

P. How was it produced?

M. The honey-sugar has a reducing effect on the cupric compound and changes it into a cuprous substance. This, however, does not form a soluble salt with tartar and must, therefore, precipitate as cuprous hydrate. Here is a larger quantity of the red substance. If I try to convert it into cuprous sulphate by pouring dilute sulphuric acid over it I can obtain none.

P. The hydrate turns quite dark, and the solution becomes greenish blue, as if it contained a cupric compound.

M. Quite right; it does. The equation is:

$$2CuOH + H_2SO_4 = CuSO_4 + Cu + 2H_2O;$$

the monovalent copper has been changed into the divalent copper and the free metal.

P. That is wonderful! We have never met with a reaction like this before.

M. No. We can explain it thus: the cuprous ion is un-

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stable in solution, and is converted into the cupric ion and copper:

$$2Cu^{\cdot} = Cu^{\cdot\cdot} + Cu.$$

Perhaps you would understand me better if you compare this with the reverse reaction, as given by iron. (P. 276.) There the ferric ion and iron change into the ferrous ion:

$$2Fe^{\cdot\cdot\cdot} + Fe = 3Fe^{\cdot\cdot}.$$

P. Yes; I see. And since it just depends on the conditions whether a reaction goes backwards or forwards, the one way is just as possible as the other.

M. Right. But if I pour hydrochloric instead of sulphuric acid on the cuprous hydroxide it does not become dark, but light, and eventually white. Cuprous chloride, CuCl, has been formed. It is a difficultly soluble salt, and so cuprous ions cannot dissolve in sufficient quantities to bring about the reaction

$$2Cu^{\cdot} = Cu^{\cdot\cdot} + Cu.$$

Conversely, we can (as in the case of iron) convert the cupric into the cuprous salt by metallic copper. I boil a solution of cupric chloride in strong hydrochloric acid with copper chips in a small flask. The liquor first becomes very dark then bright yellow. I dilute it with a large quantity of water; a snow-white precipitate is thrown down. This is CuCl.

P. I must take a little time to think that over.

M. A reaction similar to the iron one has taken place in the hydrochloric acid solution:

$$CuCl_2 + Cu = 2CuCl.$$

Such a change was made possible by the hydrochloric acid uniting at once with the cuprous chloride, and dissolving it. But on dilution with water the combination is split up, and then the cuprous chloride is thrown down. This introduces

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us to the consideration of some very remarkable circumstances connected with the equilibrium in chemical processes; you may find it interesting to examine into them when your studies are further advanced. Just now I can only show you the reactions and give you the equations.—Cuprous hydrate has an anhydride, and yields it readily, on warming. It is called cuprous oxide; abundant quantities are found in nature in various places. It is known to mineralogists as *ruby ore*, and is a valuable source of the metal. Natural copper also exists in combination with sulphur and other elements, especially iron. There are two sulphur compounds, cupric sulphide, CuS, and cuprous sulphide, Cu_2S; they correspond and are similar in composition to cupric and cuprous oxide.

P. I have met with one; it was prepared by the action of hydrogen sulphide on copper sulphate. Was it CuS?

M. Yes. It was produced from the cupric salt:

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

40. LEAD.

M. Lead is another of the metals known to the ancients and still familiar to us in every-day life. Can you tell me some of its properties?

P. It is very heavy; is softer than the other metals; and almost never has a metallic glitter, but is clouded and grey. It melts easily and is poisonous.

M. That is quite correct. Its density is 11.4, the melting-point is 330°. By scraping it with a knife we can easily see the appearance of the metal itself; it is of a grey colour, somewhat between that of iron and zinc. It becomes quickly covered with a thin layer of oxide which slowly thickens and forms a protection, as in the case of copper. It shows a special peculiarity as regards its behaviour towards air and moisture. I have here, in these two similar vessels, equal

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quantities of freshly-cut lead chips; water is poured over them, and they are shaken from time to time. Do you notice any difference?

P. Certainly. The water in one glass is much more cloudy than in the other.

M. Correct. The cloudy water has been distilled and so made pure; the other was taken from the spring. You see that lead, in the presence of air, oxidizes much more strongly in pure than in ordinary water.

P. How does the lead know which is which?

M. By the impurities in the spring-water. This contains carbonates and sulphates, both of which form difficultly soluble salts of lead. They are deposited on the metal and protect it. But with pure water the hydroxide is produced, and it does not adhere to the lead. This is an important point, because it shows that lead pipes can be used quite well for drinking and household water, but not for pure or rain-water. It is as well to know this, since lead compounds are very poisonous. Lead stands between zinc and copper in the table of electric potentials; i.e., lead salts are thrown down by zinc, but, on the other hand, they make copper compounds precipitate. The salts contain the colourless, divalent lead ion, $Pb^{\cdot\cdot}$. Lead is fairly stable towards acids; it stands just on the boundary line of those metals which expel the hydrogen from acids; on the other hand, it generally forms difficultly soluble salts. What would you use to dissolve lead?

P. Nitric a id; it dissolves most metals.

M. Good; but there is one point we must take into account. I pour concentrated nitric acid over some lead shavings; you see we obtain a weak effect which soon ceases altogether; and even on warming I can get no further result. If, however, I merely dilute with a considerable quantity of water and heat, a vigorous evolution of gas commences and the lead dissolves.

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P. Your experiments are most wonderful. They generally show that the contrary to what we should expect happens. Here you would suppose that the concentrated acid must naturally have a stronger effect than the weak solution.

M. I choose these surprising experiments on purpose to teach you to draw conclusions with caution. They help you to recognize that in each reaction a number of different conditions are co-operating. The special circumstance governing this case is as follows: the strong nitric acid first of all produces lead nitrate; but this is not soluble in the acid, and so it forms a protective covering over the metal. When we add water this protection is dissolved.

P. But I couldn't know that lead nitrate was so difficultly soluble in the concentrated acid?

M. Certainly not. But, after to-day you will assume that, as a rule, salts are less soluble in their own acids than in pure water. I have here a saturated solution of lead nitrate in water. If I pour in some nitric acid I immediately obtain a crystalline precipitate of solid nitrate of lead, although the addition of acid has increased the total volume of the solution.

P. Can you give any explanation of this?

M. It is an universal rule that *every salt is less soluble in a solution which already contains one of its ions.* I cannot tell you the reason; the subject is too advanced for you.—Now let us return to lead. You have already seen, from the solution we have just used, that the lead ion, $Pb^{\cdot\cdot}$, is colourless. It has a sweetish taste; but I would not advise you to try it, since it is very poisonous. It has a specially disagreeable property of collecting in the body, in small quantities at a time, with an accumulative effect which eventually leads to a painful and protracted illness. The lead ion most strongly resembles the barium ion in its behaviour.

P. Does the former also form a difficultly soluble sulphate?

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M. Yes. Just add some dilute sulphuric acid to our lead solution.

P. A white precipitate is immediately thrown down. It appears to settle much more quickly than the barium sulphate did.

M. That is because all lead compounds have a high density. Add some hydrochloric acid to another portion of the lead solution.

P. Here we obtain another white precipitate.

M. This is not so difficultly soluble as the sulphate; if you collect some and treat it with hot water it will dissolve. On cooling most of it will crystallize out again. Just make the experiment. It is a pretty one, for the crystals form in long, glittering needles.—Try how potassium iodide acts towards a lead solution.

P. It gives a yellow precipitate.

M. This also is much more soluble in hot than in cold water, and separates out in a peculiarly beautiful form on allowing a warm, saturated solution to cool.

P. How am I to separate the precipitate?

M. Throw the whole mixture on to a filter, let the liquid run through, wash what is left twice with pure water, then lay it on a sheet of filter-paper so that the moisture clinging to it can drain away. You would better place a piece of absorbing material, such as an ordinary wood-pulp board, underneath. Now write down the formula of these salts for me. You know that lead is divalent.

P. Lead sulphate, $PbSO_4$, lead chloride, $PbCl_2$, lead iodide, PbI_2.

M. Correct. Here is another salt, which goes by the appetizing name of *sugar of lead*, because it has a sweet taste. It is lead acetate, the acetic acid salt of lead. It is the compound of lead most in use, since it is much more easily soluble than even the nitrate. I dissolve some in water.

P. The solution is quite cloudy. Is the salt impure?

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M. The carbonic acid in the atmosphere decomposes it slightly. You know that acetic acid is a weak acid; now, carbonate of lead is a fairly stable salt, and so the carbonic acid is able to drive out the acetic acid. I filter the solution in order to make it quite clear, and then lead carbon dioxide through it.

P. A thick precipitate is produced.

M. It is carbonate of lead, $PbCO_3$. It is found as a mineral, under the name of *cerussite.* If I continue to introduce carbon dioxide all the lead is not thrown down, but after a certain quantity of acetic acid has been formed any further precipitation is prevented because the acid is then sufficiently concentrated to redissolve the carbonate of lead. The conditions here are the same as those attending the precipitation of zinc by hydrogen sulphide. (P. 154.)

P. Then none of the carbonate of lead would be thrown down if we previously added enough acetic acid?

M. Just so. Make the experiment afterwards for yourself. Carbonate of lead is an important substance. It is known in everyday life as *white lead,* and is used as a pigment by artists and as ordinary paint. Although it has several defects a substitute is not easy to find, because it gives a beautiful white colour, covers well, and forms a lasting coat.

P. Then what are its faults? Oh! Of course! It is poisonous.

M. Yes; that is the worst. But we have also to take another property into account. I have here a sheet of paper marked with white lead; I hold it for a second over the bottle containing my hydrogen sulphide solution.

P. A brown stain is produced at once. Yes; I remember that hydrogen sulphide gives a brown precipitate with lead salts.

M. Lead sulphide, PbS, has been formed. This compound is easily produced wherever white lead comes in contact with hydrogen sulphide. You know that the latter is a pro-

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duct of the decomposition of eggs and other organic sulphur compounds; therefore, white-lead paint is very apt to turn brown. Zinc-white has not this defect, for zinc sulphide itself is white. (P. 312.)

P. Then why do they not simply use nothing but zinc-white?

M. Because it does not cover so well. Lead compounds refract light very strongly and, on that account, a thin layer of paint is sufficient to hide the colour lying underneath and give everything a pure white appearance. Still, after all, it would be a good thing if the use of white lead were absolutely forbidden as a paint, for it often causes poisoning. We must now say something more about the sulphide, since it is the most important ore of lead. Here is some. It is called *galena.*

P. It does not look like the precipitate, it was brownish-black, this is grey and has an almost metallic glitter.

M. The precipitate was amorphous sulphide of lead; the mineral is crystalline. If you allow the former to crystallize it will have the same appearance.—We roast galena in order to obtain the metal.

P. I know now what that means. The ore is heated in the air so that the sulphur burns away as an oxide, and the lead is converted into oxide of lead, from which the metal is obtained by fusing with charcoal.

M. In this particular instance we are able to work more economically. We roast away only a portion of the sulphur, and afterwards heat the mixture of lead oxide and lead sulphide apart from the air. The following reaction takes place:

$$PbS + 2PbO = 3Pb + SO_2.$$

You see we here make use of the sulphur in the lead sulphide to reduce the oxide.

P. How neat that is! Can't we adopt it in other cases?

M. No; and for several reasons. It can only be carried

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out with lead. However, the preparation is not yet completed; for the crude metal, the lead-plate thus obtained, generally contains silver which must be separated and preserved. It is therefore heated on flat hearths in a strong current of air, and is thus converted into its oxide. The silver, being a noble metal (p. 315), does not combine with the oxygen; and we so arrange that the oxide of lead, which becomes melted by the heat, can flow away and leave the pure silver behind.

P. I have not yet seen any oxide of lead.

M. Here is some, just as it is obtained by the above process. It solidifies in yellowish-red scales, and is called *litharge.* You can prepare the hydroxide of lead and see if it is soluble in caustic potash or ammonia.

P. It is thrown down as a white precipitate. It is soluble in potassium hydrate, but not in ammonia.

M. Right. It dissolves in the former because it is able to act as a weak acid, like the hydroxides of aluminium and zinc. If we heat lead oxide for a considerable time it changes into this substance which I have here.

P. What a beautiful red! What is it called?

M. Minium or *red lead.* It has the formula Pb_3O_4, and is formed from the oxide by the addition of atmospheric oxygen. I pour dilute nitric acid over some of it.

P. Hulloa! It has turned dark brown. What has happened?

M. We shall see immediately. I filter off the liquid. Test it with dilute sulphuric acid.

P. A white precipitate is at once thrown down; so the lead ion must be present.

M. The nitric acid has dissolved out a portion of the lead. The equation is:

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + 2H_2O + PbO_2.$$

The brown substance is PbO_2; it is called lead dioxide. It resembles manganese dioxide in having very weak acidic prop-

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erties. (P. 289.) It has various uses in manufacturing processes, and also plays an essential part in electrical accumulators. However, I shall not go into that subject now.

P. What a pity!

M. You will learn about it later on. But to make amends, I shall show you a pretty lead salt. If I add a chromate to my lead solution, a beautiful yellow precipitate of lead chromate, $PbCrO_4$, is produced. It is called *chrome yellow*, and has a variety of uses as a pigment. We also obtain other colours varying from orange to red which, since their tints are partially due to the chromate, are severally known as *chrome orange* and *chrome red*. These paints are also poisonous, and subject to the same changes as white lead. I shall make use of the remainder of my lead acetate solution to prepare a lead-tree. I dilute it with water, and hang in it a zinc rod. The metallic lead will then separate out (p. 318) in the form of beautiful, leaf-like crystals which settle on the zinc as if growing on a tree. There is nothing particular to learn from this, except that metals can crystallize if allowed to solidify under suitable conditions. It is, moreover, a pretty experiment.

41. MERCURY.

M. You already know mercury so well that all I have to do to complete the description of its properties is only to give you a few figures. It solidifies or melts at $-39.4°$, boils at 358°, and has a density of 13.595 at 0°. At the ordinary temperature neither damp nor dry air has any effect on it, but it oxidizes at or about 300°. However, the mercuric oxide, when subjected to a greater heat, decomposes, as you know, into the metal and oxygen. Therefore, the adjective noble may be applied to mercury for all practical purposes. But if it is contaminated with any foreign metal it does not remain bright, but becomes coated with a grey skin which consists of the oxide of the extraneous substance and mer-

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cury in a fine state of division. This easily enables us to recognize whether the mercury is pure. It cannot expel hydrogen from dilute acids, but it is attacked by weak nitric acid. I pour some over a drop of mercury and warm. What do you see?

P. The usual brown vapours are given off, and a clear solution is formed. Therefore, the mercury ion is colourless.

M. Good. But I must tell you that this metal has two ions; the monovalent mercurous ion, $Hg^{\cdot}$, and the divalent mercuric ion, $Hg^{\cdot\cdot}$.

P. Has the name mercury got anything to do with the Roman god of trade and thieves?

M. Certainly. The metal was compared to that lively personage on account of its mobility. Its other designation, *quicksilver*, also expresses the same property. The chemical symbol, Hg, is, on the other hand, an abbreviation of its Greek name, *hydrargyrum*, or liquid silver. Mercurous nitrate, $HgNO_3$, is first formed on dissolving the metal in nitric acid, especially if the former is in excess. But on heating this salt with more acid, the monovalent mercurous changes into the divalent mercuric ion, and mercuric nitrate, $Hg(NO_3)_2$, is produced.

P. How can we tell which salt is present in the solution?

M. By various ways. On adding caustic soda the mercurous ion gives mercurous oxide, which has a black appearance, as you see. On the other hand, if the mercuric salt is present, mercuric oxide, which is yellow, is formed.

P. There are one or two points which I do not understand. Should not the hydroxide be precipitated in the above cases?

M. Possibly they are produced first of all; but, in each case, they immediately change into their anhydrides with loss of water. What you saw happening slowly with copper (p. 326) goes so fast with mercury that the first stage is not perceptible. Mercurous oxide is a combination of two combin-

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ing weights of mercury with one of oxygen, and, therefore, the equation for its formation is:

$$2HgOH = Hg_2O + H_2O,$$

while the divalent mercuric ion must have the hydroxide $Hg(OH)_2$, whose anhydride is mercuric oxide, HgO.

P. One other question: Why is this mercuric oxide yellow, and not red?

M. Because it is finely divided. It precipitates from a solution in water as a yellow powder, while what you saw before was prepared in another way and was in the form of red crystals.

P. Can that slight difference make such an alteration?

M. Here is a red crystal of potassium dichromate; just grind it down.

P. How strange! It has become quite yellow.

M. I shall now show you another method of distinguishing between the two mercury ions. I pour some hydrochloric acid into my nitric acid solution.

P. A white precipitate is thrown down. Where have I seen it before? It looks familiar.

M. It resembles silver chloride; that is what reminded you of it. It is mercurous chloride, but is generally known by its old name, *calomel*, which was given to it long ago. It is used in medicine, but must be taken with care; for mercury compounds are powerful poisons, and it is only because calomel is extremely difficultly soluble that it is harmless within certain limits. What is its formula?

P. Since it contains the monovalent mercury ion it must be HgCl.

M. Right. It is the most important of the mercurous salts. Of the mercuric compounds, the best known is the chloride, $HgCl_2$, which we call *corrosive sublimate*, or often, for short, *sublimate*.

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P. Sublimation is for solid substances what distillation is for liquids.

M. Yes. Mercuric chloride used to be prepared by a process, the last stage of which was a sublimation; and so, as often happens, a general term has come to be applied specifically to one particular substance.—The salt is not very soluble in water; the solution is very poisonous. An extremely dilute solution is used medicinally as a *sterilizer*, to kill harmful germs in the form of small living organisms; but we have to be cautious with it as man is particularly sensitive to mercury poisoning. On adding caustic soda to the solution I obtain a precipitate of yellow mercuric oxide.

P. Can we make it into the red variety?

M. Yes. All we have to do is to apply heat for some time until the temperature approaches the decomposition point. When I add potassium iodide to my mercuric chloride solution a beautiful red precipitate is thrown down. It easily dissolves in excess of potassium iodide producing a faint yellowish tinge in the liquid. This solution does not respond to the test for the mercuric ion; and, in particular, we can add as much hydrate of sodium or of potassium as we wish without making the oxide of mercury separate out. What conclusions do you draw?

P. The mercuric ion must have changed into some other one. But what can it be?

M. The reaction somewhat resembles the effect of potassium cyanide on a ferrous salt. (P. 281.) The red precipitate formed first was mercuric iodide, HgI_2; this unites with the excess of potassium iodide and gives a salt of the composition K_2HgI_4, whose ions are potassium and HgI_4''. The mercury has, therefore, passed into the anion and has formed a complex compound with the iodine; thus it is no longer present as a cathion, and so can no longer be precipitated as the oxide by bases.

P. In the same way that no precipitate of ferrous hydrate

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is given by adding a base to prussiate of potash solutions, though they contain iron.

M. Quite right. We shall study mercury iodide more in detail, since it also shows some remarkable properties. Here is a somewhat larger quantity of it.

P. What a magnificent red colour! Is it used by painters?

M. No. Why I do not exactly know. Perhaps as a pigment it has some defects of which I am unaware; but possibly they depend on certain phenomena which I am just about to show you. I take some of the powder and warm it cautiously in a test-tube—

P. Hulloa! That is rather startling! The whole substance has turned yellow all at once.

M. On letting it cool, the red colour does not return simultaneously with the decrease of temperature; but, in certain places, red stains form and slowly increase till, after some time, the whole becomes red, as before.

P. Then can we make it yellow again?

M. Yes; all we require to do is to warm it above 126°. If we apply greater heat than this it melts and begins to volatilize. The vapour condenses in yellow crystals on the colder portions of the glass. Just examine them closely.

P. Separate red stains are forming, as before. What is the meaning of this?

M. It has to do with a phenomena, of which you already know; I described it to you when dealing with sulphur. (P. 135.) Mercury iodide is dimorphous, i.e., it can crystallize in two different forms. One, the red variety, is stable up to 126°; the other, yellow form, exists from above this temperature to the melting-point. Therefore, on warming the red crystals above 126° they change into the yellow; and these, again, are converted back into the red, on cooling. The latter transition is a protracted one, as is very frequent (in fact, it is the rule) with solid substances.

P. What I do not understand is why are yellow and

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not red crystals deposited from the vapour onto the cold tube?

M. Because here we have another example of how the unstable form is produced first of all. I can show you this phenomenon by using this substance in another form, whereby our observations are facilitated by a complete change of colour. Mercury iodide dissolves in spirits of wine, and, on allowing the solution to evaporate slowly, separates out as the red variety, because there is ample time for the change to take place. But when I pour the spirits of wine solution into water a precipitate is formed quickly, and, as you see, not in the red form.

P. It is almost white. Why is it not yellow?

M. Merely because it is in a finely divided condition. You remember that sulphur in the same state looks white. If I place this white, milky mixture in the sunshine it turns red on that side to which the sun has access.

P. So I see. Why is that?

M. The white precipitate consists of the unstable yellow variety, and the sunshine hastens its transition into the stable red form. Light frequently has this effect of accelerating a reaction. You know that it bleaches many colours. It generally does so by oxidizing the colouring-matter by the oxygen of the air. This, of course, would happen without the aid of light, only very much more slowly. Let us now leave the iodide, and have a look at one other mercury compound, *cinnabar.*

P. I have some in my paint-box. It is a beautiful red pigment.

M. It is mercuric sulphide, HgS. I cautiously add a little hydrogen sulphide to mercuric chloride—

P. —and obtain a white precipitate.

M. I pour in more and more hydrogen sulphide, and, as you see, the precipitate turns yellow, red, brown, and finally black. That is because mercuric sulphide forms various

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compounds with chloride of mercury; they become darker the more hydrogen sulphide we add. Eventually, when the precipitate is black, we have the pure mercuric sulphide.

P. But you have just told me that this is the same as cinnabar, which is red.

M. The black variety is an amorphous form. It is of a cinnabar-red colour when in the crystalline condition. Cinnabar is found in nature as large crystals, which have rather a grey, metallic appearance; but on grinding them down we obtain the red powder. Mercuric sulphide can also be crystallized artificially. The two elements combine very easily. If I grind them in a mortar in the proportion of their combining weights I obtain a black powder, which is amorphous mercuric sulphide.

P. Is it the more unstable form of the two, since it is always produced first?

M. Yes. We can tell this by the fact that the black mercuric sulphide changes into the red of itself, i.e., without the necessity of our applying work; but the reverse transition never takes place. However, we can obtain the black from the red variety by first dissolving or vapourizing it. It sublimes fairly easily on heating, and, if the condensation is rapid the black form is deposited. But on allowing the sublimation to take place slowly we obtain the red variety.—Mercuric sulphide is the most important ore of mercury. The metal is obtained from it in various ways.

P. Can they not roast it as they do the other metallic sulphides?

M. Of course they can. The sulphur then burns to the dioxide, and the mercury is obtained in the metallic condition since it is not oxidized under these conditions. The only difficulty is that it vapourizes and mixes with the SO_2, from which it has then to be condensed by being led through large chambers or tubes. So the way they do is to heat the ore with iron; this unites with the sulphur, and the mercury

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distills away and can be much more easily condensed because the vapour is not mixed with a foreign gas. Finally, there is still another process in which the ore is heated with lime. Calcium sulphide and mercuric oxide are first formed by a double decomposition, but the latter dissociates at once into the metal and oxygen which oxidizes the organic matter usually present. By this method, also, the mercury vapour is easily condensed. In conclusion, tell me what you know of the uses of mercury?

P. It is employed for various apparatus, e.g., the barometer and thermometer. Its compounds are used in medicine. And, I think, it comes into the preparation of looking-glasses; but how, I do not know.

M. Looking-glasses are silvered with an amalgam of mercury and tin. Amalgams are alloys of mercury, which are partly liquid, partly solid. Mercury has played, and still continues to play, an important part in the development of physics and chemistry. It is a feature of the manometer or pressure-gauge, and of many important electric appliances as well as of other apparatus familiar to you. The reason of this manifold use is due to the fact that it is a noble metal (i.e., one not easily attacked chemically), a liquid and very heavy.

42. SILVER I.

M. To-day we shall talk about silver.

P. This is another universally known metal. Why did we not begin with these familiar elements? It might have made my studies easier. I do not say that they have been particularly difficult, but it took me all my time to master them.

M. We could not have done other than we did. For in order to discuss the compounds of silver I have to assume that you know about oxygen, chlorine, sulphur, and a whole host of other non-metals.

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P. True. The metals are not of much importance by themselves; and even if we wish to discover how they are obtained we must have some knowledge of the other elements.—Well, I know that silver is a noble metal, white in colour, has a glitter, and is pretty expensive. Why is that?

M. Simply because it is not very abundant. It is, as a rule, not expensive to prepare it from its ores if they are pure. But they seldom are. On account of its value it is sought for in places where it is present even in small quantities, and then it is naturally more expensive to obtain it. Silver, as you know it in the coinage and household effects, is, however, not pure; it contains $^1/_{10}$ of copper. The pure metal is too soft and would be too easily scratched and bent; the copper makes it harder. Do you remember under what atmospheric conditions silver loses its polish? (P. 133.)

P. Yes. If hydrogen sulphide or sulphur is present.

M. Right. Most of the ores of silver are sulphur compounds. Moreover, white silver with a metallic glitter is not the only form of this element. If we precipitate it from a solution of its salts by zinc and other less noble metals, we procure it in various forms from grey to black in colour. Indeed, under special conditions, it can be obtained as a colloid in solution in water. This has a reddish-brown to greyish-brown appearance, according to circumstances, and is used in medicine. Silver is not soluble in dilute acids; but dissolves in nitric acid, forming silver nitrate.

P. I already know of this substance as a test for the chlorine ion. (P. 90.) The solution is water-clear, so the silver ion is colourless.

M. Quite right. Silver forms only one series of compounds; its ion, $Ag^{\cdot}$, being monovalent, like those of the alkali metals.

P. But the connection between them must be very remote.

M. It is nearer than one would think; various sodium compounds have the same crystalline form as the correspond-

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ing silver salts.—I must also tell you that the silver ion is very poisonous.

P. How can that be? We are continually using silver spoons and dishes.

M. You should be able to understand why. Silver is a noble metal; so its disposition and capability to change into its ion is very slight; and it gets no opportunity at all of doing so when in household use. Besides, the chlorine ion is present everywhere in our bodies, and it unites with silver and forms the difficultly soluble, and therefore harmless, silver chloride. Silver only acts as a poison if we absorb it into the system in its ion state; but it is then so powerful that silver nitrate was called by the old chemists *lapis infernalis* (the diabolical stone). It is known to us as *lunar caustic.*

P. I remember that I once had my finger cauterized with a stick of lunar caustic. The place afterwards became quite black.

M. That was due to the action of light which decomposes most compounds of silver, especially in the presence of organic matter. By this agency metallic silver of a black colour is made to separate out. We shall deal with this property later on, for photography, i.e., sun pictures, depends on this effect. The nitrate, $AgNO_3$, is the best known of the salts of silver. It crystallizes in large, water-free crystals, which are extremely soluble in water. The solution gives a neutral, not an acid, reaction as most salts of the heavy metals do. This shows that silver hydrate is a strong base.

P. Because, otherwise the water would partially split up the salts into acid and base.

M. Right. Moreover, silver hydrate behaves in the same way as the corresponding mercury compound: the product obtained by drying down the precipitate given by caustic soda has the formula of the anhydride, silver oxide, Ag_2O. I add some sodium hydrate to a nitrate of silver solution—

P. Is this brown precipitate oxide of silver?

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M. Yes. It is a fairly unstable substance. If I heat some of it when dry in a test-tube oxygen soon evolves and white silver remains behind in a spongy form. This decomposition is much more easily effected than that of mercuric oxide.

P. So silver is still more noble than mercury?

M. That is so; for silver oxide is never produced from the metal and atmospheric oxygen at any temperature. If, however, oxygen is allowed to act on spongy silver at a high pressure and under definite conditions we can make them unite. Of the other salts of silver you already know the appearance of its halogen compounds.

P. Yes; all three are difficultly soluble. Silver chloride is white; so is the bromide; but the iodide is yellow. They are always thrown down when the silver ion is brought in contact with a halogen ion.

M. Right. These salts are much more stable than the oxide. We can heat all three in the air, without decomposing them. They melt easily. Solid chloride of silver is not brittle, as are most salts, but can be pared and cut with a knife like a piece of horn. Mineralogists call this salt in its natural state *horn silver.* In chemical laboratories a quantity of silver chloride usually collects from the various analyses; it is desirable to convert this again into other silver compounds. I shall show you how that can be easily done. This pan now contains chloride of silver; I add dilute hydrochloric acid and place a zinc rod in the center of the mixture. You see, a band of grey silver is already forming round the zinc. By to-morrow even the chloride of silver round the very edge of the dish will have been reduced. What is happening here?

P. If the zinc is converting the chloride of silver into the metal it must be combining with the chlorine. Therefore, since zinc is divalent, we have:

$$2AgCl + Zn = 2Ag + ZnCl_2.$$

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You nod; so that is correct. But, please, explain to me how the zinc can have an effect on the silver chloride round the edges? It does not reach there.

M. If you take into account the fact that the reduction does not take place within the chloride of silver, but spreads outwards from the zinc, you will be able to see the reason. The zinc first attacks the chloride with which it is in direct contact in the usual manner. But it then sets up a galvanic cell with the silver and the silver chloride, and an electric current is produced. This leads the chlorine ion of the silver chloride to the zinc, and so metallic silver and chloride of zinc are formed. The process is quite similar to the action of a Daniell's battery. (P. 319.)

P. Are we able to prove that there actually is an electric current?

M. Quite easily. For instance, take the point which caused you astonishment and made you ask the question; namely, the fact that zinc can exert a reducing effect at places with which it is not in contact. It does this only through the instrumentality of the current. The silver, which has already turned into the metallic state, serves as the conductor and thus makes the reduction of the chloride possible. You can make the following experiment: Wrap the zinc in filter-paper so that it does not come in contact at all with the silver chloride, and lead a wire, preferably of platinum or silver, from the zinc into the silver chloride solution; then you will find a deposit of grey, metallic silver round the wire, not round the zinc.

P. Because the electric current enters at the wire?

M. No; it makes its exit there: for the positive stream goes from the silver through the wire to the zinc. If you break the wire and connect the ends with a galvanometer, you can at once detect a current by the needle becoming diverted.—We shall now learn something about the circumstances attending the solubility of silver chloride.

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P. I remember that somewhat over $^1/_{1000}$ g. dissolves in 1 litre.

M. Quite right; 0.0015 g. But on adding ammonia, a large quantity goes into solution. Here is a glass in which silver chloride has been precipitated from silver nitrate by sodium chloride; you see the addition of ammonia gives an absolutely clear solution. Why?

P. I suppose the ammonia forms a new complex ion with the silver ion.

M. Yes; your supposition is correct. The new compound has the composition $Ag(NH_3)_2$. Silver chloride also dissolves in sodium thiosulphate. (P. 215.) That, likewise, is due to the formation of a new ion; but this time, however, it is an anion which consists of the thiosulphate ion and silver. We are not yet quite certain regarding its composition, because several compounds of the same nature are apparently formed all at one time; but we are sure of the main fact. Make the experiment for yourself.

P. Yes; it dissolves in a second.

M. This reaction is of importance to photographers; we shall refer to it later on when dealing with their methods.

P. Are we going to take an actual photograph?

M. To be sure we are. It will be the means of teaching us a good deal of chemistry. But let us now consider for a short time the other halogen compounds of silver. You have already met with the bromide; it is much more difficultly soluble than silver chloride, as is evidenced by the fact that though it dissolves freely in sodium thiosulphate ammonia absorbs only a small quantity.

P. I cannot understand how there can be any difference in the solubility since, in each case, it is the silver ion which is removed.

M. That is just the point. The silver ion is not taken away down to the last remnants by the ammonia; but a certain very minute quantity remains behind. This quan-

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tity is so small that it need not be taken into account when considering the solubility of chloride of silver, but it must be recognized when dealing with silver bromide. I have already told you that a salt is less soluble in a solution which contains one of its ions; well, this applies in the case of silver bromide.

P. And how about sodium thiosulphate?

M. It is quite a good solvent of bromide of silver, because it absorbs the silver ion much more freely than ammonia does. In other words, it leaves such a slight quantity of silver ion behind that the remnant has very little effect on the solubility of the bromide of silver. On the other hand, it is quite otherwise with silver iodide; it is much more difficultly soluble even than silver bromide itself; it is not dissolved by ammonia at all to any appreciable extent, and only in slight quantities by sodium thiosulphate. However, it dissolves readily in potassium cyanide.

P. What is the reaction in that case?

M. You have already seen examples of similar ones. First of all, let us make some experiments. I add a little potassium cyanide to my silver solution—

P. A precipitate is thrown down. It is just like silver chloride.

M. It is silver cyanide, AgCN. When I pour in more potassium cyanide the precipitate dissolves, and the solution no longer responds to the test for silver; no change occurs on adding either sodium chloride or caustic soda.

P. It is just as happens with the iron in a prussiate of potash salt.

M. Quite right. The reaction is quite similar:

$$AgCN + KCN = KAg(CN)_2;$$

i.e., the potassium salt of the silver cyanide ion, $Ag(CN)_2'$, has been formed. A solution of this salt retains a smaller

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quantity of silver ion than the thiosulphate solution does, and, therefore, the following reaction takes place when iodide of silver is added to potassium cyanide:

$$AgI + 2KCN = KAg(CN)_2 + KI;$$

or if we simply write the ions:

$$Ag^{\cdot} + 2CN' = Ag(CN)_2'.$$

See if the dots and strokes are correct. (P. 291.)

P. On the left we have one dot and two strokes, leaving one stroke over; on the right we have one stroke. They are quite correct.

M. The solution of this salt, potassium silver cyanide, is also of industrial importance. It is used when they wish to silver any articles made of other metals by the electroplating process; because when the silver is made to separate out on the cathode by the electric current it is deposited in a polished and not so crystalline a condition as it is precipitated from, for example, a nitrate of silver solution. A large number of our household effects are treated by this method, and so a great industry has been founded on this chemical property. There is just one other point. What are the ions of this salt?

P. $K^{\cdot}$ and $Ag(CN)_2'$.

M. You see that the potassium, not the silver, travels to the cathode. The fact that silver separates out there is due to a secondary reaction. (P. 70.)

P. Ah! I remember! The potassium cannot exist as such, so its presence must be apparent in some other form. In our previous instance it made the water part with its hydrogen.

M. In this case it expels the silver from the silver cyanide ion thus:

$$K + KAg(CN)_2 = Ag + 2KCN.$$

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It is the silver which separates out, and we have two potassium cyanide instead of the potassium silver cyanide. At the anode, which is made of silver, the following reaction occurs:

$$Ag(CN)_2 + Ag = 2AgCN;$$

i.e., two silver cyanide are formed there; and if the liquid is kept in motion they unite with the product formed at the cathode and form potassium silver cyanide again:

$$2KCN + 2AgCN = 2KAg(CN)_2;$$

so the solution keeps at the same concentration, just as we had in the case of the copper sulphate. (P. 324.)

P. Does not the silver cyanide separate out before it can be mixed, since it is so difficultly soluble?

M. No; for they always keep an excess of potassium cyanide in the bath.

43. SILVER II. PHOTOGRAPHY.

M. I have arranged a special treat for you to-day: you shall learn about photography.

P. I have long wished to, but I thought it would be too difficult.

M. Things are difficult or easy, according to the degree of perfection we wish to attain. So far as making a pretty picture is concerned that is not hard to manage. To begin with, here is a plate such as is used for receiving the image; it is, of course, useless for its intended purpose, as it has been exposed to the light.

P. It is a sheet of glass, covered on one side with a coating which has somewhat the appearance of solidified cream.

M. This is composed of gelatine impregnated with finely divided bromide of silver. In order to prepare it they add to a warm solution of gelatine first ammonium bromide

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and then, in the dark, silver nitrate in such quantities that the mixture contains a little excess of the bromide. By this means we obtain a precipitate of silver bromide, which at first acts very slowly, i.e., it requires a great deal of light in order to produce a picture. On longer heating it becomes more sensitive, and the workmen have certain tests by which they tell when the mixture is ready. It is then allowed to cool so that the gelatine sets to a solid, which is afterwards cut up into strips and put to soak.

P. Why?

M. In order to eliminate the excess of potassium bromide and the ammonium nitrate formed in the reaction, since these are deleterious. It is, then, again liquefied by heat and poured onto the glass plates, where it solidifies and dries. These are the silver bromide gelatine dry plates The whole process must be carried out in the dark or in red light.

P. Why red light?

M. Because it has the least effect on the plates. However, they now use a machine which does all the work without any inspection being necessary. I have such a plate in this case, which is called a dark-slide. It has a shutter in front which can be drawn out when I wish to take a picture with my camera. Do you know what a camera is?

P. Yes. An inverted image of the object is obtained inside it with the help of the lens.

M. Your description will be sufficient for our present purpose. The lens is fixed on the front of the camera. Since a sharp image is only obtained when the lens is in a certain position I have to use a different focus according to the distance of the subject to be photographed. But in landscapes there is one fixed position which is correct for all distant views. The lens is now covered with its cap, the dark-slide put into position, the shutter drawn, and the cap removed for one second.

P. How much time ought we to allow?

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M. It depends on the lens and on the light. The simple cameras, which can be bought fairly cheap, are generally so constructed that, in sunshine and out of doors, a correct exposure is given by simply pressing down a button. In summer, a second or two, and longer, may be necessary if the day is dull. I have photographed the view through the open window; we have now to go and develop the plate.—

P. I can see nothing here in this red light.

M. Your eyes will soon get accustomed to it. Since I have to take out the plate and work with it, no light that can affect it ought to be admitted. If you do not possess a dark room you must wait till nightfall. I first of all pour the developer into a shallow dish.

P. What is the developer?

M. It is a mixture of several substances, and has the property of reducing the silver bromide, i.e., of converting it into metallic silver and the bromine ion. You cannot yet understand the chemical reactions, since they have to do with organic substances; however, all that I now tell you is quite sufficient to begin with. The bromide of silver has the special property of becoming reduced at the places where the light has fallen on it, the more quickly the stronger the light. Just look at the plate through the developer. The red light naturally gives it a red appearance.

P. Part of the plate is becoming black.

M. That is where the image of the sky fell. The brightest light was there, and there the first precipitation of black silver takes place. But now you see that black lines and stains are forming everywhere. They are the other features in the picture.

P. I cannot recognize any.

M. Because this is a negative, i.e., the light parts are dark, and so everything is the reverse of what it is in reality: white objects show black, the black are white. I continue the development until almost the whole picture has become dark.

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I then rinse the plate and lay it in another dish containing a solution of sodium thiosulphate (1 part in 5 parts of water).

P. What is the effect of this?

M. You know that it dissolves silver bromide, but not metallic silver. Therefore, the whole of the bromide of silver, which still remains on the plate, is removed, and an impression in black silver is all that is left.

P. The plate has become quite black.

M. When it has become quite clear on the lower side the solution is completed. The plate is again washed, and can now be exposed to daylight.—Let me hold it up to the window. Do you recognize anything?

P. Is that blackness at the top the sky? Ah! Now I see the house, and the trees beyond, and the pavement beneath them. And there are also some people, but they are very small. That is splendid!

M. We have still to wash the plate free from sodium thiosulphate: I lay it in a dish and let water run slowly over it. It must be left like this for at least half an hour. And here you must bear in mind that the gelatine film has now become swollen and is very liable to be injured; the plate must be grasped by the edge and handled as little as possible. After it has been washed it is stood upright and left to dry. This takes several hours, for no heat ought to be used, as the gelatine might liquefy and the whole picture would then dissolve off the plate.

P. It is a nuisance to have to wait so long.

M. I have brought another negative, which I prepared some days ago; so you shall now see how we obtain the picture. We (as they say) print it. For this purpose we use a paper that can be bought ready made. There are two varieties; ordinary printing-out paper, and bromide paper which requires to be developed. The former is coated with (among various other substances) chloride of silver, and has the property of darkening in the light,—as you know silver chlo-

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ride always does. (P. 90.) The latter has a coating similar to that on the silver bromide plate, but much less sensitive; it only requires a short exposure to the light and is then developed like a negative. Let us take the silver chloride paper first. The negative is placed in a printing-frame (something like a picture-frame), into which it is fixed by means of a back that can be held against it by springs. First of all the negative is placed in the frame with the coated side inwards, on this is laid a sheet of the sensitive paper with its coated side downwards, and then the back of the frame is inserted, the whole being securely clamped together by the springs.

P. Why is the back in two divisions?

M. In order to enable us to see when the printing is finished. One of the springs is released, part of the back is lifted on the hinge, the paper underneath is examined, and everything can be made secure again afterwards without disturbing the relative position of negative and paper. I lay the frame in sunshine. Meanwhile we can take a print from another negative on bromide paper.

P. Then we shall need to use the dark-room again?

M. That is not necessary. The paper is so slightly sensitive that it can be handled in a dark corner of this room; but, of course, we must work as quickly as we can. A sheet of the paper is inserted in the frame with the negative in exactly the same way as before, only I close the envelope immediately so that the bromide paper inside does not lie exposed and become destroyed by the light. The frame is then brought to the window for about ten seconds (the length of exposure necessary is generally noted on the envelope), and we then return to our dark corner to develop the print.

P. Let me see what the picture is like.

M. There is nothing to be seen, just as the exposed plate shows no image. We lay the paper, with the coated

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side upwards, in a dish; moisten it with water; pour the developer rapidly over it; and the picture appears almost at once.

P. Hurrah! There it is! What a good one!

M. I pass it quickly into a dish containing dilute acetic acid in order to stop the development. It is next immersed in sodium thiosulphate, as the negative was; is washed; dried; and is then ready. As you see, this photo is too black, —a sign that I have given it too long an exposure to the light. You can afterwards print another and give only half the exposure; perhaps that will be sufficient.

P. But what has happened to the other print?

M. Let us see. It is just right.

P. It appears to me to be much too dark.

M. It tones down during the after-treatment, so we must print it darker than it ought to be. I first of all put it into tap-water.

P. What causes this milkiness?

M. The paper contains silver nitrate which dissolves and forms silver chloride with the chlorine ion present in all natural waters. I now lay it in the thiosulphate solution in order to remove the excess of silver salt.

P. The picture is quite yellow.

M. There is nothing but silver there, just as there was on the developed plate; only the metal is now in another form; it is amorphous and has a brown colour. Since this tint is not pretty the photograph must be "toned" by treatment with gold.

P. What effect has that?

M. Finely divided gold has a bluish-violet appearance. The print is immersed in a solution containing a gold salt. Since gold is more noble than silver it is precipitated by the latter and is deposited in the place of the silver. You see that as the picture lies in the solution it slowly changes in colour and becomes more and more violet. When we

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obtain the tone we wish we remove the photo, wash it, and let it dry. Now this print is also finished.

P. There is more work in this than in the previous process.

M. To be sure; but the result is better. If you afterwards compare the two photographs you will find that in the silver chloride print the details are more distinctly defined. I ought to tell you that, for the sake of clearness, I have shown you the successive treatments in a different order from the usual one; the gold toning ought to be done immediately after washing the printed picture, and the "fixing" last of all. But then the change of colour is not so strikingly obvious.

P. How long ought the final washing to last?

M. For one hour, in running water. Otherwise, you must wash for two hours, and change the water every 10 or 15 minutes.

P. I would like to have the formulæ for all these solutions.

M. I would advise you to buy them ready made to begin with, because you will then be certain that any mistake you may make does not lie in their preparation. However, you may prepare the thiosulphate from the solid salt; take 1 part to 5 parts of water. If your father should think of giving you a camera and photographic materials he should begin by getting you a cheap apparatus carrying small plates from about 9 to 12 cm. square; for you will first spoil a fair number before you obtain good results. Remember just to make only one or two exposures as a start, and develop them as soon as possible. That will help you to recollect the conditions under which you were working; and so if you find you have made a mistake you can correct it next time. After some practice you can refer to a larger text-book on photography and make up your own solutions. When you are expert in these details you might even try to prepare the plates; for though this would hardly lead to any saving in economy, it would teach you much that is interesting.

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44. TIN.

M. Tin was also known to the ancients. It is not found in the metallic condition in nature, but is readily procured from its oxide which is prevalent and easily obtained. Describe the properties of this metal.

P. It is whiter than lead; preserves its polish in the air; and melts at a low temperature. It is fairly soft.

M. Correct. Its melting-point is 235°. In the table of electric potentials it stands between zinc and lead and near to the latter; it is, therefore, in this sense not a particularly noble metal, and its behaviour when exposed to a damp atmosphere is due to a transparent coating of oxide (as is the case with aluminium) which prevents any further oxidation. Formerly, many household fittings were made of pure tin; but on account of its softness these were for ornament only. Tin is, however, employed in large quantities to cover other metals, and also in alloys.

P. Yes; I know; we cover iron sheets with tin and call it *white metal.*

M. Quite right. And we, likewise, tin copper cooking utensils, for copper is poisonous and easily soluble in acid and fatty foods; while tin resists these much better and is not poisonous. Cooling apparatus for the condensation of the vapour in the preparation of distilled water is also made of tin or has a tin lining, for this metal is unaffected by pure as well as by ordinary (drinking) water.

P. Then what really are the impurities in ordinary stream- or spring-water?

M. They vary slightly according to the rocks through which the water has passed. It is quite customary to find the ions of sodium, calcium, magnesium, chlorine and sulphate. The carbonate ion is seldom absent; and if a little free carbonic acid is not present the water tastes insipid.

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P. How does it happen that pure distilled water has a taste, while impure stream-water has none? At least I cannot detect any. It should be the very reverse!

M. It is simply because we are accustomed to drink stream, and not distilled, water. A sensation experienced again and again in the same way eventually becomes quite imperceptible.

P. Yes; that is so. A miller only hears his mill when the clapper is silent.

M. As we should suppose from its position in the table of electric potentials tin dissolves only very slowly in dilute but better in concentrated acids. I place a piece of silver-paper in a test-tube, and pour hydrochloric acid over it. On commencing to warm we obtain a vigorous evolution of hydrogen.

P. What is this silver-paper?

M. It is tin in the form of a thin film. It is used as an easy and simple means of protecting articles from the atmosphere by wrapping them in it. The metal is impenetrable; and if it is well rolled round and round practically no air can enter or escape.

P. So that is why it is placed round chocolate, cheese, and other food-stuffs. I always thought that it was only because the wrapping looked like silver.

M. The silver-paper has now dissolved. The liquid contains the divalent stannous (from *stannum*, the Latin name for tin) ion, $Sn^{\cdot\cdot}$. There are, moreover, a series of stannic compounds in which the tin is tetravalent. I shall tell you about them later on. As you see, the stannous ion is colourless. With hydrogen sulphide solution, it gives a brown precipitate of stannous sulphide or sulphide of tin, SnS; we shall have something to say about this substance afterwards. With caustic soda we obtain a white precipitate of stannous hydroxide, $Sn(OH)_2$, which dissolves in excess of the alkali, and therefore has weak acid properties. Our tin solution is

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a strong reducing agent; of course, because the divalent stannous ion changes into the tetravalent tin. I add some mercuric chloride to the stannous chloride; you see that, first of all, a white substance is thrown down; it turns grey on warming. What do you think has happened?

P. Mercuric chloride is $HgCl_2$; on reduction it must lose chlorine. That explains the white precipitate: it was mercurous chloride, HgCl. But the grey?

M. Well; what must happen if more chlorine is removed from the calomel?

P. Mercury will be left. But it should look like a sparkling drop.

M. The grey substance really is mercury; but it has separated out in such small particles that we cannot detect the glitter of the separate units with the naked eye. On allowing the glass to stand a little longer in a warm place the minute drops will gradually coagulate into larger ones, and then we can recognize them as ordinary mercury. I rub some of the grey substance on a sheet of copper—

P. —which becomes polished, like silver.

M. It has formed an amalgam with the mercury. Here is some of the compound obtained by evaporating a solution of tin in hydrochloric acid. It is much used in dyeing processes under the name of *salts of tin*; we call it stannous chloride. It contains water of crystallization and has the formula $SnCl_2+2H_2O$. Dissolve some in water!

P. It dissolves very fast, but the solution remains cloudy.

M. That is the result of the reducing properties. It absorbs oxygen from the air and changes into difficultly soluble tetravalent tin compounds. In order to keep a stannous solution always efficacious for laboratory use we add hydrochloric acid and let some metallic tin, say tinfoil, lie in it.

P. I understand; the effect is the same as that obtained with the iron on p. 276.

M. Quite right. Compounds containing the stannic ion,

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$Sn^{\cdots\cdot}$, are little known. The hydrate of the tetravalent tin, $Sn(OH)_4$, behaves like an acid. The tetrachloride of tin does not look at all like a salt. Here is some.

P. This is a water-clear liquid!

M. It is obtained by heating tin in a stream of chlorine; this liquid then distills over. It boils at 120°, a temperature only slightly higher than the boiling-point of water.

P. The glass in which you have it has been sealed up. Is that to prevent it evaporating?

M. No. It is because tetrachloride of tin fumes strongly in the air and decomposes.

P. Does it become more highly oxidized?

M. No. It does not react with the oxygen, but with the water vapour. It is decomposed into hydrochloric acid and stannic hydroxide, according to the equation:

$$SnCl_4 + 4H_2O = Sn(OH)_4 + 4HCl.$$

Here is a glass containing a little of the tetrachloride; I scratch the neck with a glass-cutter, break it off cautiously, and pour the contents into water—

P. How it fumes! The watery solution is quite clear. Is the hydroxide soluble?

M. It has dissolved in a partially colloidal form. If we put the solution to stand aside for some time a precipitate gradually separates out, because the hydrate changes into a denser form. However, a portion is still present in the ion condition, for when I pour in hydrogen sulphide I obtain a yellow precipitate of tin disulphide, SnS_2. By cautiously adding caustic soda the stannic hydrate first separates out and then dissolves readily in more of the alkali hydrate; it is, therefore, known as stannic acid, and its salts as stannates. The solution contains sodium stannate:

$$2NaOH + Sn(OH)_4 = Na_2SnO_3 + 3H_2O.$$

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However, we are here entering on a complicated subject, so we had better leave these substances until a later stage of your studies. What formula will the anhydride have?

P. $Sn(OH)_4 = SnO_2 + 2H_2O$.

M. Correct. This coincides with the formula of silicon dioxide; and, indeed, tin and silicon resemble each other in many respects. Tin dioxide is found in nature; it is called *tin-stone*, and is the chief ore of tin. It is easily prepared as a grey powder (it is white when pure) by heating the metal in the air; this product is called *tin-ashes*, and is used as a metal-polish. It is readily reduced again to tin by charcoal or hydrogen.

P. You said you would show me something with sulphide of tin.

M. So I shall. Here is a solution of sodium sulphide Na_2S, the sodium salt of hydrogen sulphide. You remember that we could prepare the sulphides of the metals of the iron group from their salts with it, but not with hydrogen sulphide by itself—

P. Because the product then became dissolved again by the acid formed in the reaction. (P. 157.)

M. Good. However, as you see, I have now precipitated tin disulphide from an acid solution with hydrogen sulphide; so it is one of the difficultly soluble sulphides. And if I pour sodium sulphide over the yellow precipitate—

P. It dissolves. That is peculiar. I have never seen anything like this before.

M. The sodium sulphide has combined with the tin disulphide and has formed a salt, Na_2SnS_3:

$$Na_2S + SnS_2 = Na_2SnS_3.$$

P. Where have I seen just such another formula?

M. You must be thinking of the formula for sodium stannate, Na_2SnO_3. In fact, both correspond; only we here have three sulphur in the place of three oxygen. The substances

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themselves are similar; both are salts; their ions are sodium and, on the one hand, SnO_3''; on the other, SnS_3''. There is a great number of such salts and ions which contain sulphur instead of oxygen; they have been given the names of the corresponding oxygen compounds, with the insertion of the prefix *thio* (from the Greek word for sulphur). Thus the salt here produced is called sodium thiostannate; and the ion, SnS_3'', is the thiostannate ion.

P. Why did I never get the opportunity of learning about these substances before this?

M. Because the metals previously dealt with form none. You must remember that, in addition to tin, there are gold, platinum, and a number of still other metals, of which you will only gain a knowledge as time goes on. The above reaction is, moreover, an important test for tin, and serves in analysis as a means of separating it from other metals.—I now add hydrochloric acid to my sodium thiostannate solution, and you see, we again obtain a yellow precipitate of tin disulphide. Just try to write the equation.

P. Two sodium require two hydrochloric acid, so:

$$Na_2SnS_3 + 2HCl = 2NaCl + SnS_2. \ldots\ldots$$

Now, what remains over? Two hydrogen and one sulphur,—these form hydrogen sulphide. But no gas was given off?

M. Just smell! It has remained in solution because there was sufficient water present.

P. Yes; I see, or rather smell, how it is.

M. This reaction only appears to deviate from the general rule. What would you expect to obtain by the action of hydrochloric acid on a salt?

P. The acid of the salt.

M. Yes; and this must have the formula H_2SnS_3, according to the equation:

$$Na_2SnS_3 + 2HCl = 2NaCl + H_2SnS_3.$$

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But such an acid is not stable; it decomposes immediately into hydrogen sulphide and tin disulphide, just as carbonic acid splits up into water and carbon dioxide.

P. I now see, for the first time, how great is the similarity between the thio and the oxygen compounds. Hydrogen sulphide here takes the place of the water there.

M. Just so. I decompose some of my stannous chloride solution with hydrogen sulphide; dark brown stannous sulphide, SnS, is thrown down. I pour some sodium sulphide over it.

P. It does not dissolve.

M. So it cannot form a thio salt. I pour off the sodium sulphide, and take instead another solution of sodium sulphide, which has stood over powdered sulphur and has, therefore, become yellow by dissolving some.

P. It dissolves the stannous sulphide.

M. Now add hydrochloric acid!

P. The precipitate is yellow, not brown.

M. This is the explanation: the dissolved sulphur has united with the stannous sulphide and thus made the formation of sodium thiostannate possible:

$$Na_2S + SnS + S = Na_2SnS_3.$$

That this is what actually happens is proved by the yellow precipitate. It is, moreover, a universal rule that many of the metals which we have previously mentioned form thio salts only from the compounds that are rich in sulphur; and, therefore, those that contain little are hardly soluble at all in ordinary sodium sulphide, but dissolve readily in the yellow solution containing sulphur.

P. I thought I knew by this time the most important of the reactions common to metals; but I find that there is always something fresh to learn!

M. You will often be surprised in this way. I have, to

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be sure, shown you several beautiful experiments and explained many an interesting circumstance; but they are, after all, a very small proportion of those which lie before you. Do not think that you have exhausted the whole of chemistry with this general introduction which I am now giving you. Even were a man to devote all his life to its study he would fail to reach its limits.

45. GOLD AND PLATINUM.

M. Gold and platinum stand at the opposite extremity of the table of electric potentials from the alkali metals. The latter are obtained from their compounds with the greatest difficulty, and at the first chance make all haste to enter again into combination. But gold and platinum, on the contrary, do not combine readily with other elements. They persist in the free state under all sorts of circumstances; and when a compound is once formed it takes every opportunity of decomposing into its elements. One sign of this is that gold and platinum are found in nature only in the metallic condition, or at least alloyed with other metals, but never in combination as salts.

P. Then I shall not have much chemistry to learn about them.

M. We ought not to say that. They resemble nitrogen, which forms compounds with difficulty, but still is present in many substances. The chemistry of gold, and especially of platinum, is somewhat involved; yet it has some special peculiarities which I would not like you to miss. Let us take gold first. Tell me its properties.

P. It is yellow; takes a good polish, which it keeps on exposure to the air; is very heavy; and is the most expensive of metals.

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M. The last is not correct; there are much more costly metals among the rarer chemical products. But on account of its scarcity it is certainly the most expensive of those metals familiar to mankind since early days. For this reason it is of especial acceptance as coinage, and nearly all the countries throughout the world have, one by one, adopted gold as the standard of their monetary system.

P. It surely does not matter whether they take gold or silver?

M. Certainly it does; for the relative value of the two metals does not remain the same from year to year. Some time ago much less silver, as compared with gold, could be obtained than at the present day; and, therefore, we could buy, for the same quantity of gold, much less silver then than now. Both metals thus have a standard of value of their own, each of which alters variably; so we can use either the one or the other, but not both simultaneously. The gold supply is, on the whole, more regular than that of silver; and on this account gold is the better standard. As I said, gold is always found in nature in the free condition, and all we have to do is to separate the heavy metal (density = 19.3) by mechanical means from the lighter sand with which it is mixed.

P. How did it get into the sand?

M. It came there with the quartz when the rocks crumbled away. In early times they knew of no other method than to wash it out, i.e., the auriferous sand was shaken up with water, which was then poured off; it carried away the light sand with it and left the heavy gold lying on the bottom of the dish. However, the metal is often in such a fine state of division that it is taken away with the sand. In such a case they treat the mixture with mercury, which easily dissolves gold. The metal is thus washed out, just as we extracted sugar from sand with water. (I. p. 14.)

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P. And is the solvent afterwards evaporated in order to obtain the gold?

M. The mercury is distilled off so that none may be lost. Since more recent times such finely divided gold has been caught without using mercury as the removing agent. A very dilute solution of potassium cyanide is employed; this chemically dissolves the metal, though what actually happens you can only learn later on. Gold is not attacked by acids, not even by nitric acid, but is soluble in a mixture of nitric and hydrochloric acids because of the chlorine set free; for the hydrogen of the hydrogen chloride is oxidized by the oxygen of the nitric acid. The mixture is known as *aqua regia* (the kingly water), because it dissolves gold, the king of metals. I throw a small leaf of gold into some chlorine water; you see it dissolves pretty soon giving a yellow liquid.

P. So the gold ion is yellow, as the metal is?

M. Yes. This solution contains gold trichloride, $AuCl_3$; gold is therefore trivalent. We know few of the other salts of this ion, for gold separates out from its solutions very easily into the metallic condition. I add a little green copperas to my gold solution—

P. What a curious colour!

M. It is the gold, which has separated out in a very finely divided state; it looks blue by transmitted light, but a reflected ray has something of the gold, almost an auburn colour. Let me take another reducing agent, stannous chloride (p. 361), instead of the ferrous sulphate.

P. This time we get another colour, a reddish-purple.

M. Here the gold is in a still finer state of subdivision; it is in solution in the colloidal form. After some time stannic acid precipitates out and takes the gold with it. This precipitate is called *golden purple;* it retains its colour when melted up in glass, and, therefore, serves as a pigment for porcelain ware.—It is obtained from the yellow solution of

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gold trichloride as a difficultly crystallizable, brown mass. Much prettier crystals are produced if we add the chloride of either sodium or potassium. The salt then formed has the composition $NaAuCl_4$, (or $KAuCl_4$). It may be looked upon either as a compound of the alkali chloride with gold chloride, e.g., $NaCl+AuCl_3$, or as the alkali salt of a complex gold chloride ion, $AuCl_4'$. The latter theory is the correct one.

P. How did they find that out?

M. Simply by electrolyzing the salt. If the gold travels to the anode then it is present in the anion; otherwise, it must be in the cathion. I have mentioned this compound to you especially because the sodium salt is the "gold" used by photographers in toning their prints. (P. 357.) They make up a solution of about 1 in 1000, and add a little chalk in order to remove the harmful effect of any free acid which may be present.—Finally, we have potassium gold cyanide, $KAu(CN)_4$. It is analogous to the above compounds, and is formed by the action of a dilute potassium cyanide solution on finely divided gold if we take care to let the oxygen of the air afford the necessary oxidation. This reaction is the one by which we obtain the metal when it is present in small quantities. (P. 368.)

P. Is the gold oxidized in this case by the oxygen of the air? If so, how can it be called a noble metal?

M. You have touched on a question to which no satisfactory reply can be made within the scope of our present work, though science is able to give a complete and sufficient answer. The gold cyanide ion, $Au(CN)_4'$, which is contained in the salt, is a very stable substance, and only an extremely minute trace of the gold ion splits off from it; so this small amount is all that does not yield to the oxidation process. In other words, gold behaves as a noble metal only if the conditions are such that any compounds it may be able to form can easily decompose again. When it gets

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the opportunity of producing a strong compound, as in the case of potassium gold cyanide, its power to return to the free condition ceases and it behaves much less as a noble metal. This explanation must be sufficient for you to-day. Now let us turn to platinum.

P. I already know a good deal about this element. It is a somewhat grey, shining metal which almost nothing can attack. It is, therefore, used for all sorts of apparatus, especially in electrolysis. It is very difficult to melt. Moreover, it can act catalytically.

M. Right. Like gold, it exists in nature only in the metallic state. It also is obtained by a mechanical washing process, but the product is mixed with other metals of a similar nature.

P. What! Are there many more like platinum?

M. There are six altogether; but platinum is present in far greater abundance than the others, and so is the most important as far as technical and scientific purposes are concerned. In order to procure the pure metal we have to dissolve the crude platinum ore in aqua regia; the solution contains chloro-platinic acid, H_2PtCl_6.

P. Then gold acts somewhat differently from this?

M. Not very. Gold, when dissolved in aqua regia (not in chlorine-water), is always present as chloro-auric acid, $HAuCl_4$, on account of the excess of hydrochloric acid in the solution:

$$AuCl_3 + HCl = HAuCl_4.$$

The formula is different from that of the platinum acid; but, otherwise, the compounds are the same. The platinum is thrown down from its acid solution by ammonium chloride, in the form of ammonium chloro-platinate $(NH_4)_2PtCl_6$, which separates out as a difficultly soluble, yellow precipitate consisting of microscopic crystals.

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P. I think I remember having heard before of some substance like this.

M. Yes; it was the potassium salt, K_2PtCl_6, which is used as a test for potassium. (P. 224.) It is very similar in composition to the ammonium salt. The latter, which is called *platinum sal ammoniac*, can be changed into metallic platinum simply by applying heat; for all the other constituents are volatile and so escape. Since the residual metal does not melt it remains of a grey and dull appearance; it is called spongy platinum. This form has specially strong catalytic properties.

P. Why is that?

M. The catalytic effect resides on the surface where the metal has contact with the gases. Therefore, the greater the area a given quantity of platinum has the greater will be the effect. Any other means that would increase the available surface would have the same result. I twist some scraps of ammonium chloro-platinate round a thin platinum wire and heat cautiously so that the sponge remains clinging to the wire. I have now a fulminating pellet at the end. I hold it in a stream of gas from my hydrogen apparatus (I. p. 140, Fig. 25); it glows; and, with a bang, the hydrogen commences to burn.

P. That is just like an instrument for lighting the gas, which I saw quite recently.

M. It depends on exactly the same phenomenon. The hydrogen (or the coal-gas) mingles, as it streams out, with the oxygen of the air and forms an explosive mixture. The constituents unite, owing to the catalytic agency of the platinum, to form water, and the heat given out makes the sponge red-hot. A thin wire is essential if we wish the gaseous mixture to ignite; when we have the sponge by itself it will glow; but there will be no ignition. Why this should be I do not know.

P. Surely it must be possible to find out?

M. Certainly; but so far no one has done so. In virtue

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of the catalytic effect which platinum shows in many other gaseous reactions, it has, especially within recent days, risen into great prominence. You remember, I drew such phenomena to your notice at various times.

P. Yes. You told me that they offered a wide field of research. I used to wish that I was far enough advanced to undertake their investigation.

M. You have certainly much yet to learn before you can make the attempt. We must now bring these conversations on chemistry to a close. I shall be very glad if they have been the means of making you long to learn more of this beautiful science.

P. Yes; I would willingly continue its study. I feel sorry that the long vacation has come, and that I shall meet no more with the strange and wonderful things which chemistry has to show.

M. You ought to go over all you have learned, and so make certain about what you know.

P. I thought you would say that. But this would not be nearly so pleasant as to see something quite new, which I could then consider quietly and with an open mind. Tell me, could I not get some book to read as a preparation for my future studies?

M. I see; your talk about preparation is merely an excuse to find out what lies beyond. However, I have no objections to make; self-chosen work usually gives not only more pleasure, but better results than a set task. At the present day we are rather awkwardly situated as regards chemical text-books. During the last fifteen years a great change has sprung up in our views and acceptance of science, and most of our literature is written in accordance with earlier ideas. I have directed your studies along the lines of modern thought, and to unlearn them by changing to the old style would cause you a great deal of unnecessary difficulty. So there is really only one book that I can recommend to you

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as being quite up to date: it is "Outlines of Inorganic Chemistry." W. Engelmann, Leipzig, 1904. The subject-matter is a good deal more difficult than what you have been accustomed to; but it will answer many of the questions whose explanations I have, so far, had to reserve.

P. That is just the book I want.

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